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QUANTITATIVE CHEMICAL ANALYSIS

By the same Author.

QUALITATIVE CHEMICAL ANALYSIS.

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QUANTITATIVE

CHEMICAL ANALYSIS

BY

DR. C. REMIGIUS FRESENIUS

PRIVY AULIC COUNSELLOR;
DIRECTOR OF THE CHEMICAL LABORATORY AT WIESBADEN;
PROFESSOR OF CHEMISTRY, PHYSICS, AND TECHNOLOGY
AT THE WIESBADEN AGRICULTURAL INSTITUTE.

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PREFACE.

It is now ten years since the publication of the last translated edition of this Work, and the changes in quantitative analysis during this period have necessitated an entire revision of every part of the book.

The present Volume, though only the first instalment of the Work, is complete in itself, and to render it more useful I have added an Index, which has been carefully prepared, and is believed to be as full as it can practically be made.

A translation of the Second Volume will follow as soon as the German original is ready. A summary of its contents will be found on p. 6.

The old notation is retained in our translation by the express wish of the Author, who states that he shares with the highest authorities in Germany, "a most firm conviction that for Inorganic Chemistry it is the simplest and the best."

A. V.

LONDON, *March*, 1876.

CONTENTS.

PAGE
INTRODUCTION 1

PART I.

GENERAL PART.

DIVISION I.

EXECUTION OF ANALYSIS.

SECTION I.

Operations, § 1 9
  I. Determination of quantity, § 2 9
    1. Weighing, § 3 9
      a. The balance 9
          Accuracy, § 4 10
          Sensibility, § 5 11
          Testing, § 6 and § 7 12
      b. The weights, § 8 15
      c. The process of weighing, § 9 16
          Rules, § 10 18
    2. Measuring, § 11 19
      a. The measuring of gases, § 12 20
          Correct reading off, § 13 22
          Influence of temperature, § 14 25
          Influence of pressure, § 15 25
          Influence of moisture, § 16 26
      b. The measuring of fluids, § 17 27
        α. Measuring vessels graduated for holding.
          aa. Vessels serving to measure out one definite volume of fluid.
              1. Measuring flasks, § 18 27
          bb. Vessels serving to measure out different volumes of fluid.
              2. The graduated cylinder, § 19 29
        β. Measuring vessels graduated for delivering.
          aa. Vessels serving to measure out one definite volume of fluid.
              3. The graduated pipette, § 20 29
          bb. Vessels serving to measure out different volumes of fluid.
              4. The burette.
                I. MOHR's burette, § 21 31
                II. GAY-LUSSAC's burette, § 22 . . . 36
                III. GEISSLER's burette, § 23 37

PAGE
II. Preparation of substances for the processes of quantitative analysis.
  1. Selection of the sample, § 24 37
  2. Mechanical division, § 25 38
  3. Drying, § 26 40
    Desiccators, § 27 41
    Water-baths, § 28 43
    Air-baths, § 29 47
    Oil-baths, § 30 49
    Drying-disk, § 31 50

III. General procedure in quantitative analysis, § 32. 51
  1. Weighing the substance, § 33 52
  2. Estimation of water, § 34 53
    a. Estimation of water by loss of weight, § 35 54
    b. Estimation of water by direct weighing, § 36 . . . 56
  3. Solution of substances, § 37 58
    a. Direct solution, § 38 58
    b. Solution, preceded by fusion, § 39 59
  4. Conversion of the dissolved substance into a weighable form, § 40. 59
    a. Evaporation, § 41 60
      Weighing of residues, § 42 65
    b. Precipitation, § 43 67
      α. Separation of precipitates by decantation, § 44 . 68
      β. Separation of precipitates by filtration 69
        aa. Ordinary filtration, § 45.
          αα. Filtering apparatus 69
          ββ. Rules in filtering 71
          γγ. Washing, § 46 72
        bb. Filtration by suction, § 47 74
      γ. Separation of precipitates by decantation and filtration, § 48 79
      Further treatment of precipitates, § 49 80
        aa. Drying of precipitates, § 50 80
        bb. Ignition of precipitates, § 51. 82
          First method, § 52 84
          Second method, § 53 86
  5. Volumetric analysis, § 54 87

SECTION II.

Reagents, § 55.
  A. Reagents for gravimetric analysis in the wet way.
    I. Simple solvents, § 56 90
    II. Acids and halogens.
      a. Oxygen acids, § 57 91
      b. Hydrogen acids and halogens, § 58 92
      c. Sulpho-acids 93
    III. Bases and metals.
      a. Oxygen bases and metals.
        α. Alkalies, and
        β. Alkaline earths, § 59 93
        γ. Heavy metals and oxides of heavy metals, § 60 . 94
      b. Sulpho-bases 95
    IV. Salts.
      a. Salts of the alkalies, § 61 95
      b. Salts of the alkaline earths, § 62 97
      c. Salts of the oxides of the heavy metals, § 63 . . . 98

B. Reagents for gravimetric analysis in the dry way, § 64 . . . 99
C. Reagents for volumetric analysis, § 65 102
D. Reagents for organic analysis, § 66 106

SECTION III.

Forms and combinations in which substances are separated from each other, or weighed, § 67 111

A. Bases.

FIRST GROUP.
1. Potassa, § 68 112
2. Soda, § 69 114
3. Ammonia, § 70 116

SECOND GROUP.
1. Baryta, § 71 118
2. Strontia, § 72 120
3. Lime, § 73 121
4. Magnesia, § 74 123

THIRD GROUP.
1. Alumina, § 75 126
2. Sesquioxide of chromium, § 76 127

FOURTH GROUP.
1. Oxide of zinc, § 77 128
2. Protoxide of manganese, § 78 130
3. Protoxide of nickel, § 79 133
4. Protoxide of cobalt, § 80 134
5. Protoxide; and 6. Sesquioxide of iron, § 81 136

FIFTH GROUP.
1. Oxide of silver, § 82 139
2. Oxide of lead, § 83 141
3. Suboxide of mercury; and 4. Oxide of mercury, § 84 144
5. Oxide of copper, § 85 146
6. Teroxide of bismuth, § 86 148
7. Oxide of cadmium, § 87 150

SIXTH GROUP.
1. Teroxide of gold, § 88 151
2. Binoxide of platinum, § 89 152
3. Teroxide of antimony, § 90 152
4. Protoxide of tin; and 5. Binoxide of tin, § 91 154
6. Arsenious acid; and 7. Arsenic acid, § 92 155

B. Acids.

FIRST GROUP, § 93 159

SECOND GROUP, § 94 166

THIRD GROUP, § 95 168

SECTION IV.

PAGE
Determination of bodies, § 96 169
I. Estimation of the bases.

FIRST GROUP.
1. Potassa, § 97 171
2. Soda, § 98 175
3. Ammonia, § 99 177
4. (Lithia), § 100 181

SECOND GROUP.
1. Baryta, § 101 182
2. Strontia, § 102 184
3. Lime, § 103 185
4. Magnesia, § 104 189

THIRD GROUP.
1. Alumina, § 105 191
2. Sesquioxide of chromium, § 106 194
3. (Titanic acid), § 107 196

FOURTH GROUP.
1. Oxide of zinc, § 108 197
2. Protoxide of manganese, § 109 201
3. Protoxide of nickel, § 110 207
4. Protoxide of cobalt, § 111 210
5. Protoxide of iron, § 112 213
6. Sesquioxide of iron, § 113 221
7. (Sesquioxide of uranium), § 114 229

FIFTH GROUP.
1. Oxide of silver, § 115 231
2. Oxide of lead, § 116 241
3. Suboxide of mercury, § 117 248
4. Oxide of mercury, § 118 249
5. Oxide of copper, § 119. 253
6. Teroxide of bismuth, § 120 262
7. Oxide of cadmium, § 121 265
8. (Protoxide of palladium), § 122 267

SIXTH GROUP.
1. Teroxide of gold, § 123 268
2. Binoxide of platinum, § 124 270
3. Teroxide of antimony, § 125 272
4. Protoxide of tin; and 5. Binoxide of tin, § 126 277
6. Arsenious acid; and 7. Arsenic acid, § 127 281
8. (Molybdic acid), § 128 288

II. Estimation of the acids.

FIRST GROUP.
First division.
1. Arsenious and arsenic acids, § 129 290
2. Chromic acid, § 130 290
Supplement: Selenious, sulphurous, hyposulphurous, iodic, and nitrous acids, § 131 295

PAGE

Second division.

Sulphuric acid, § 132 298
Supplement: Hydrofluosilicic acid, § 133 304

Third division.

1. Phosphoric acid.
   I. Determination, § 134 305
   II. Separation from the bases, § 135 314
2. Boracic acid, § 136 320
3. Oxalic acid, § 137 324
4. Hydrofluoric acid, § 138 326

Fourth division.

1. Carbonic acid, § 139 330
2. Silicic acid, § 140 346

SECOND GROUP.

1. Hydrochloric acid, § 141 354
   Supplement: Free chlorine, § 142 360
2. Hydrobromic acid, § 143 362
   Supplement: Free bromine, § 144 365
3. Hydriodic acid, § 145 365
   Supplement: Free iodine, § 146 369
4. Hydrocyanic acid, § 147 373
5. Hydrosulphuric acid, § 148 380

THIRD GROUP.

1. Nitric acid, § 149 390
2. Chloric acid, § 150 403

SECTION V.

Separation of bodies, § 151 405

I. SEPARATION OF BASES FROM EACH OTHER.

FIRST GROUP.

Separation of the alkalies from each other, § 152 407

SECOND GROUP.

I. Separation of the oxides of the second group from those of the first, § 153 413
II. Separation of the oxides of the second group from each other, § 154 418

THIRD GROUP.

I. Separation of the oxides of the third group from the alkalies, § 155 423
II. Separation of the oxides of the third group from the alkaline earths, § 156 424
III. Separation of the oxides of the third group from each other, § 157 428

FOURTH GROUP.

I. Separation of the oxides of the fourth group from the alkalies, § 158 428
II. Separation of the oxides of the fourth group from the alkaline earths, § 159 430

PAGE
III. Separation of the oxides of the fourth group from those of the third and from each other, § 160 433
IV. Separation of sesquioxide of iron, alumina, protoxide of manganese, lime, magnesia, potassa, and soda, § 161 . . . 449

FIFTH GROUP.
I. Separation of the oxides of the fifth group from those of the preceding four groups, § 162 456
II. Separation of the oxides of the fifth group from each other, § 163 463

SIXTH GROUP.
I. Separation of the oxides of the sixth group from those of the first five groups, § 164 473
II. Separation of the oxides of the sixth group from each other, § 165 485

II. SEPARATION OF ACIDS FROM EACH OTHER.

FIRST GROUP, § 166 495

SECOND GROUP.
I. Separation of the acids of the second group from those of the first, § 167 501
Supplement: Analysis of compounds containing sulphides of the alkali metals, carbonates, sulphates, and hyposulphites, § 168 . 503
II. Separation of the acids of the second group from each other, § 169 504

THIRD GROUP, § 170.
Separation of the acids of the third group from those of the first two groups, and from each other 514

INTRODUCTION.

As we have already seen in the Introduction to my "Qualitative Analysis,"—to which the present work may be regarded as the sequel—Chemical Analysis comprises two branches, viz., qualitative analysis, and quantitative analysis; the object of the former being to ascertain the nature, that of the latter to determine the amount, of the several component parts of any compound.

By qualitative analysis we convert the unknown constituents of a body into certain known forms or combinations; and we are thus enabled to draw correct inferences respecting the nature of these unknown constituents. Quantitative analysis attains its object, according to circumstances, often by very different ways; the two methods most widely differing from each other, are analysis by weight, or gravimetric analysis, and analysis by measure, or volumetric analysis.

Gravimetric Analysis has for its object to convert the known constituents of a substance into forms or combinations which will admit of the most exact determination of their weight, and of which, moreover, the composition is accurately known.

These new forms or combinations may be either educts—*i.e.*, bodies which were present as such in the analysed substance (such as water in crystallized sulphate of soda, or charcoal in gunpowder), or they may be products, *i.e.*, bodies which have been formed from the constituents of the analysed substance by the addition of other elements (such as carbonic acid and water by the combustion of paraffin, or sulphate of baryta by the mixture of chloride of barium with sulphuric acid). In the former case, the ascertained weight of the eliminated substance is the direct expression of the amount in which it existed in the compound under examination; whilst in the latter case, the quantity in which the eliminated constituent was originally present in the analysed compound, has to be deduced by calculation from the quantity in which it exists in its new combination.

The following example will serve to illustrate these points:—Suppose we wish to determine the quantity of mercury contained in the chloride of that metal; now, we may do this, either by precipitating the mercury in the metallic state from the solution of the chloride, say by means of protochloride of tin; or we may attain our object by precipitating the solution by sulphuretted hydrogen, and weighing the precipitated sulphide of mercury. 100 parts of chloride of mercury consist of 73·82 of mercury and 26·18 of chlorine; consequently, if the process is conducted with absolute accuracy, the precipitation of

100 parts of chloride of mercury by protochloride of tin will yield 73·82 parts of metallic mercury. With equally exact manipulation the other method yields 85·634 parts of sulphide of mercury. Now, in the former case we find the number 73·82 directly; in the latter case we have to deduce it by calculation:—(100 parts of sulphide of mercury contain 86·207 parts of mercury; how much mercury do 85·634 parts contain?)

$$100 : 85{\cdot}634 :: 86{\cdot}207 : x \text{—} x = 73{\cdot}82.$$

As already hinted, it is absolutely indispensable that the forms into which bodies are converted for the purpose of estimation by weight should fulfil two conditions, first, they must be capable of being weighed exactly, secondly, they must be of known composition; for it is quite obvious, on the one hand, that accurate quantitative analysis must be altogether impossible if the substance the quantity of which it is intended to ascertain, does not admit of correct weighing; and, on the other hand, it is equally evident, that if we do not know the exact composition of a new product, we lack the necessary basis of our calculation.

Volumetric Analysis is based upon a very different principle from that of gravimetric analysis—viz., it effects the quantitative determination of a body, by converting it from a certain definite state to another equally definite state, by means of a fluid of accurately known power of action, and under circumstances which permit the analyst to mark with rigorous precision the exact point when the conversion is accomplished. The following example will serve to illustrate the principle of this method:—Permanganate of potassa added to a solution of sulphate of protoxide of iron acidified with sulphuric acid, immediately converts the protoxide of iron to sesquioxide; the permanganic acid, which is characterized by its intense color, yielding up oxygen and changing to protoxide of manganese, which combines with the sulphuric acid present to colorless sulphate of protoxide of manganese. If, therefore, to an acidified fluid containing protoxide of iron, we add, drop by drop, a solution of permanganate of potassa, its red color continues for some time to disappear upon stirring; but at last a point is reached when the coloration, imparted to the fluid by the last drop added, remains: this point marks the termination of the conversion of the protoxide of iron to sesquioxide.

Now, by accurately determining the strength or power of action of the solution of permanganate of potassa—which is done simply by making it act upon a known quantity of protoxide of iron in solution, and correctly noting how much of it is required to effect the conversion of that protoxide to the state of sesquioxide—we are now able with this solution to determine the exact amount of protoxide of iron present in any solution. Thus, we will assume, for instance, that we have found it takes exactly 100 parts of our solution of permanganate of potassa to oxidize 2 parts of protoxide of iron; if now, in testing, with this standard solution of permanganate of potassa any solution containing an unknown quantity of protoxide of iron we find that 100 parts of our standard fluid are required to oxidize the iron, we know at once that the examined fluid contained exactly 2 parts of protoxide of iron; if 50 parts are required, we know that 1 part of protoxide of iron was present, and so on. Accordingly, by simply measuring the quantity used of our standard solution of permanganate of potassa, we arrive at once at an accurate knowledge of the amount of protoxide of iron.

As the process of measuring is mostly adopted, in preference to that of weighing, for determining the quantity used of the standard fluid, we give to this analytical method the name of volumetric analysis. It generally leads to the attainment of the object in view with much greater expedition than gravimetric analysis.

To this brief intimation of the general purport and object of quantitative analysis and the general mode of proceeding in analytical researches, I have to add that certain qualifications are essential to those who would devote themselves successfully to the pursuit of this branch. These qualifications are, 1, theoretical knowledge; 2, skill in manipulation; and 3, strict conscientiousness.

The preliminary knowledge required consists in an acquaintance with qualitative analysis, the stoïchiometric laws, and simple arithmetic. Thus prepared, we shall understand the method by which bodies are separated and determined, and we shall be in a position to perform our calculations, by which, on the one hand, the formulæ of compounds are deduced from the analytical results; and on the other hand, the correctness of the adopted methods is tested, and the results obtained are controlled.

To this knowledge must be joined the ability of performing the necessary practical operations. This axiom generally holds good for all applied sciences, but if it is true of one more than another, quantitative analysis is that one. The most extensive and solid theoretical acquirements will not enable us, for instance, to determine the amount of common salt present in a solution, if we are without the requisite dexterity to transfer a fluid from one vessel to another without the smallest loss by spirting, running down the side, &c. The various operations of quantitative analysis demand great aptitude and manual skill, which can be acquired only by practice. But even the possession of the greatest practical skill in manipulation, joined to a thorough theoretical knowledge, will still prove insufficient to insure a successful pursuit of quantitative researches, unless also combined with a sincere love of truth and a firm determination to accept none but thoroughly confirmed results.

Every one who has been engaged in quantitative analysis knows that cases will sometimes occur, especially when commencing the study, in which doubts may be entertained whether the result will turn out correct, or in which even the operator is positively convinced that it cannot be quite correct. Thus, for instance, a small portion of the substance under investigation may be spilled, or some of it lost by decrepitation; or the analyst may have reason to doubt the accuracy of his weighing; or it may happen that two analyses of the same substance do not exactly agree. In all such cases it is indispensable that the operator should be conscientious enough to repeat the whole process over again. He who is not possessed of this self-command, who shirks trouble where truth is at stake, who would be satisfied with mere assumptions and guess-work, where the attainment of positive certainty is the object, must be pronounced just as deficient in the necessary qualifications for quantitative analytical researches, as he who is wanting in knowledge or skill. He, therefore, who cannot fully trust his work, who cannot swear to the correctness of his results, may indeed occupy himself with quantitative analysis by way of practice, but he ought on no account to publish or use his results as if they were positive, since such proceeding could not conduce to his own advantage, and would certainly be mischievous as regards the science.

The domain of quantitative analysis may be said to extend over all matter—that is, in other words, anything corporeal may become the object of quantitative investigation. The present work, however, is intended to embrace only the substances used in pharmacy, arts, trades, and agriculture. Quantitative analysis may be subdivided into two branches—viz., analysis of mixtures, and analysis of chemical compounds. This division may appear at first sight of very small moment, yet it is necessary that we should establish and maintain it, if we would form a clear conception of the value and utility of quantitative research. The quantitative analysis of mixtures too has not the same aim as that of chemical compounds; and the method applied to secure the correctness of the results in the former case is different from that adopted in the latter. The quantitative analysis of chemical compounds also rather subserves the purposes of the science, whilst that of mixtures belongs to the practical purposes of life. If, for instance, I analyse the salt of an acid, the result of the analysis will give me the constitution of that acid, its combining proportion, saturating capacity, &c.; or, in other words, the results obtained would enable me to answer a series of questions of which the solution is important for the theory of chemical science. But if, on the other hand, I analyse gunpowder, alloys, medicinal mixtures, ashes of plants, &c., I have a very different object in view; I do not want in such cases to apply the results which I may obtain to the solution of any theoretical question, but I want to render a practical service either to the arts and industries, or to some other science. If in the analysis of a chemical compound, I wish to control the results obtained, I may do this in most cases by means of calculations based on stoïchiometric data, but in the case of a mixture a second analysis is necessary to confirm the correctness of the results afforded by the first.

The preceding remarks clearly show the immense importance of quantitative analysis. It may, indeed, be averred that chemistry owes to this branch its elevation to the rank of a science, since quantitative researches have led us to discover and determine the laws which govern the combinations and transpositions of the elements. Stoïchiometry is entirely based upon the results of quantitative investigations; all rational views respecting the constitution of compounds rest upon them as the only safe and solid basis.

Quantitative analysis, therefore, forms the strongest and most powerful lever for chemistry as a science, and not less so for chemistry in its applications to the practical purposes of life, to trades, arts, manufactures, and likewise in its application to other sciences. It teaches the mineralogist the true nature of minerals, and suggests to him principles and rules for their recognition and classification. It is an indispensable auxiliary to the physiologist; and agriculture has already derived much benefit from it; but far greater benefits may be predicted. We need not expatiate here upon the advantages which medicine, pharmacy, and every branch of industry derive, either directly or indirectly, from the practical application of its results. On the other hand, the benefit thus bestowed by quantitative analysis upon the various sciences, arts, &c., has been in a measure reciprocated by some of them. Thus whilst stoïchiometry owes its establishment to quantitative analysis, the stoïchiometric laws afford us the means of controlling the results of our analyses so accurately as to justify the reliance which we now generally place on them. Again, whilst quantitative analysis has advanced the progress of arts and industry, our manufacturers in return supply us with the most perfect platinum, glass, and porcelain vessels, and with articles of india-rubber, without which it would be next to impossible to conduct our analytical operations with the minuteness and accuracy which we have now attained.

Although the aid which quantitative analysis thus derives from stoïchiometry, and the arts and manufactures, greatly facilitates its practice, and although many determinations are considerably abbreviated by volumetric analysis, it must be admitted, notwithstanding, that the pursuit of this branch of chemistry requires considerable expenditure of time. This remark applies especially to those who are commencing the study, for they must not allow their attention to be divided upon many things at one time, otherwise the accuracy of their results will be more or less injured. I would therefore advise every one desirous of becoming an analytical chemist, to arm himself with a considerable share of patience, reminding him that it is not at one bound, but gradually, and step by step, that the student may hope to attain the necessary certainty in his work, the indispensable self-reliance which can alone be founded on one's own results. However mechanical, protracted, and tedious, the operations of quantitative analysis may appear to be, the attainment of accuracy will amply compensate for the time and labour bestowed upon them; whilst, on the other hand, nothing can be more disagreeable than to find, after a long and laborious process, that our results are incorrect or uncertain. Let him, therefore, who would render the study of quantitative analysis agreeable to himself, from the very outset endeavor, by strict, nay, scrupulous adherence to the conditions laid down, to attain correct results, at any sacrifice of time. I scarcely know a better and more immediate reward of labor than that which springs from the attainment of accurate results and perfectly corresponding analyses. The satisfaction enjoyed at the success of our efforts is surely in itself a sufficient motive for the necessary expenditure of time and labor, even without looking to the practical benefits which we may derive from our operations.

The following are the substances treated of in this work :—

I. METALLOIDS.

Oxygen, Hydrogen, Sulphur, [Selenium,] Phosphorus, Chlorine, Iodine, Bromine, Fluorine, Nitrogen, Boron, Silicon, Carbon.

II. METALS.

Potassium, Sodium, [Lithium,] Barium, Strontium, Calcium, Magnesium, Aluminium, Chromium, [Titanium,] Zinc, Manganese, Nickel, Cobalt, Iron, [Uranium, Thallium,] Silver, Mercury, Lead, Copper, Bismuth, Cadmium, [Palladium,] Gold, Platinum, Tin, Antimony, Arsenic, [Molybdenum].

I have divided my subject into three parts. In the first, I treat of quantitative analysis generally; describing, 1st, the execution of analysis; and, 2nd, the calculation of the results obtained. In the second, I give a detailed description of several special analytical processes. And in the third, a number of carefully selected examples, which may serve as exercises for the groundwork of the study of quantitative analysis.

The following table will afford the reader a clear and definite notion of the contents of the whole work:—

I. GENERAL PART.

A—Execution of Analysis.

1. Operations.
2. Reagents.
3. Forms and combinations in which bodies are separated from others, or in which their weight is determined.
4. Determination of bodies in simple compounds.
5. Separation of bodies.
6. Organic elementary analysis.

B—Calculation of the Results.

II. SPECIAL PART.

1. Analysis of waters, and more especially of mineral waters.
2. Analysis of such minerals and technical products as are most frequently brought under the notice of the chemist; including methods for ascertaining their commercial value.
3. Analysis of the ashes of plants.
4. Analysis of soils.
5. Analysis of manures.
6. Analysis of atmospheric air.

III. EXERCISES FOR PRACTICE.

APPENDIX.

1. Test experiments.
2. Tables for the calculation of analytical results.

PART I.

GENERAL PART.

DIVISION I.

THE EXECUTION OF ANALYSIS.

SECTION I.

OPERATIONS.

§ 1.

Most of the operations performed in quantitative research are the same as in qualitative analysis, and have been accordingly described in my work on that branch of analytical science. With respect to such operations I shall, therefore, confine myself here to pointing out any modifications they may require to adapt them for application in the quantitative branch; but I shall, of course, give a full description of such as are resorted to exclusively in quantitative investigations. Operations forming merely part of certain specific processes will be found described in the proper place, under the head of such processes.

§ 2.

I. Determination of Quantity.

The quantity of solids is usually determined by weight; the quantity of gases and fluids in many cases by measure; upon the care and accuracy with which these operations are performed, depends the value of all our results; I shall therefore dwell minutely upon them.

§ 3.

1. Weighing.

To enable us to determine with precision the correct weight of a substance, it is indispensable that we should possess, 1st, a good balance, and 2nd, accurate weights.

a. The Balance.

Fig. 1 represents a form of balance well adapted for analytical purposes. Although the theory of the balance belongs to the province of Natural Philosophy, there are several points in connexion with it which every analyst should understand, so that he may be able to test the instrument, and may avoid mistakes in his weighing. Experience has shown me that many young chemists do not possess sufficiently clear views on the subject.

The usefulness of the balance depends upon two points; 1st, its *accuracy*, and 2nd, its *sensibility* or *delicacy*.

§ 4.

The accuracy of a balance depends upon the following conditions :—

a. The axis or the edge on which the beam rests must lie above the centre of gravity of the balance.

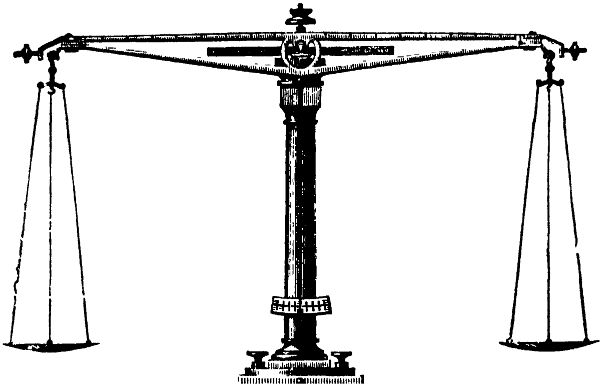

Fig. 1.

This is in fact a condition essential to every balance. If the centre of gravity fell in the axis, the beam would not oscillate, but remain in any position in which it were placed, assuming the scales to be equally loaded. If the axis be placed below the centre of gravity, the balance will be overset by the slightest impulse. When the axis is above the centre of gravity the balance represents a pendulum, the length of which is equal to that of the line uniting the point of support with the centre of gravity, and this line forms right angles with the beam in whatever position the latter may be placed. Now if we impart an impetus to a ball suspended by a thread, the ball, after having terminated its vibrations, will invariably rest in its original perpendicular position under the point of suspension. It is the same with a properly adjusted balance—impart an impetus to it, and it will oscillate for some time, but it will invariably return to its original position; in other words, its centre of gravity will finally fall back into its perpendicular position under the point of support, and the beam must consequently reassume the horizontal position.

But to judge correctly of the force with which this is accomplished, it must be borne in mind that a balance is not a simple pendulum, but a compound one, *i.e.*, a pendulum in which not one, but many material points move round the turning point. The inert mass to be moved is accordingly equal to the sum of these points, and the moving force is equal to the excess of the material points below, over those above the axis.

β. The points of suspension of the scales must be in a plane with the axis. If the axis be placed below the line joining the points of suspension, increased loading of the scales will continually tend to raise the centre of gravity of the whole system, so as to bring it nearer and nearer the axis; the weight which presses upon the scales combining in the relatively high-placed points of suspension. At last, when the scales have been loaded to a certain degree, the centre of gravity will shift altogether to the axis, and the balance will consequently cease to vibrate; any further addition of weight will finally overset the beam by placing the centre of gravity above the axis. If, on the other hand, the axis be placed above the line joining the points of suspension, the centre of gravity will become more and more depressed in proportion as the loading of the scales is increased; the line of the pendulum will consequently be lengthened, and a greater force will be required to produce an equal turn; in other words, the balance will grow less sensitive the greater the load. But when the three edges are in one plane, increased loading of the scales will, indeed, continually tend to raise the centre of gravity towards the axis, but they can in this case never actually join, and consequently the balance will never altogether cease to vibrate upon the further addition of weight, nor will its sensibility be lessened; on the contrary—speaking theoretically—a greater degree of sensibility is imparted to it. This increase of sensibility is, however, compensated by other circumstances. (See § 5.)

γ. The beam must be sufficiently rigid to bear without bending the greatest weight that the construction of the balance admits of; since the bending of the beam would of course depress the points of suspension below the axis, and this would, as we have just seen, tend to diminish the sensibility of the balance in proportion to the increase of the load. It is, therefore, necessary to avoid this fault by a proper construction of the beam. The form best adapted is that of an isosceles obtuse-angled triangle, or of a rhombus.

δ. The arms must be of equal length, i.e., *the points of suspension of the scales must be equidistant from the axis*, for if the arms are of unequal length, the balance will not be in equilibrium supposing the scales to be loaded with equal weights, but there will be preponderance on the side of the longer arm.

§ 5.

The sensibility of a balance depends principally upon the three following conditions :—

a. The friction of the edges upon their supports must be as slight as possible. The friction of the edges upon their supports depends upon the form and material of those parts of the balance. The edges must be made of good steel, the supports may be made of the same material; it is better, however, that the centre edge at least should rest upon agate planes. To form a clear conception of how necessary it is that even the end edges should have as little friction as possible, we need simply reflect upon what would happen were we to fix the scales immovably to the beam by means of rigid rods. Such a contrivance would at once altogether annihilate the sensibility of a balance, for if a weight were placed upon one scale, this certainly would have a tendency to sink; but at the same time the connecting rods being compelled to form constantly a right angle with the beam, the weighted scale would incline inwards, whilst the other scale would turn outwards, and thus the arms would become unequal, the shorter arm being on the side of the weighted scale, whereby the tendency of the latter to sink would be immediately compensated. The more considerable the friction becomes at the end edges of a balance, the more the latter approaches the state just now described, and consequently the more is its sensibility impaired.

β. The centre of gravity must be as near as possible to the axis. The nearer they are, the shorter becomes the pendulum. If we take two balls, the one suspended by a short and the other by a long thread, and impart the same impetus to both, the former will naturally swing at a far greater angle from the perpendicular than the latter. The same must of course happen with a balance; the same weight will cause the scale upon which it is placed to turn the more rapidly and completely, the shorter the distance between the centre of gravity and the axis. We have seen above, that in a balance where the three edges are on a level with each other, increased loading of the scales will continually tend to raise the centre of gravity. A good balance will therefore become more delicate in proportion to the loading of the scales, but, on the other hand, its sensibility will be diminished in about the same proportion by the increment of the mass to be moved, and by the increased friction; in other words, the delicacy of a good balance will remain the same whatever may be the load placed upon it. The nearer the centre of gravity lies to the axis, the slower are the oscillations of the balance. Hence in regulating the position of the centre of gravity we must not go too far, for if it approaches the axis too nearly, the operation of weighing will take too much time.

γ. The beam must be as light as possible. The remarks which we have just now made will likewise show how far the weight of the beam may influence the sensibility of a balance. We have seen that if a balance is not actually to become less delicate on increased loading, it must in one respect have a tendency to become more delicate by the continual approach of the centre of gravity to the axis. Now it is evident, that the more considerable the weight of the beam is, the less will an equal load placed upon both scales alter the centre of gravity of the whole system, the more slowly will the centre of gravity approach the axis, the less will the increased friction be neutralized, and consequently the less sensibility will the balance possess. Another point to be taken into account here is, that the moving forces being equal, a lesser mass or weight is more readily moved than a greater. (§ 4 *a*).

§ 6.

We will now proceed, first, to give the student a few general rules to guide him in the purchase of a balance; and, secondly, to point out the best method of testing its accuracy and sensibility.

1. A balance able to bear 70 or 80 grammes in each scale, suffices for most purposes.

2. The balance must be enclosed in a glass case to protect it from dust. This case ought to be sufficiently large, and its sides should not approach too near the scales. It must be constructed in a manner to admit of its being opened and closed with facility, and thus to allow the operation of weighing to be effected without any disturbing in-

fluence from currents of air. Therefore, either the front part of the case should consist of three parts, viz., a fixed centre part and two lateral parts, opening like doors ; or, if the front part is made of one piece which slides up and down, the two sides of the case must each be provided with a door.

3. The balance must be provided with a proper contrivance to render it immovable whilst the weights are being placed upon the scale. This is most commonly effected by an arrangement which enables the operator to lift up the beam and thus to remove the middle edge from its support, whilst the scales remain suspended; older contrivances fix the scales, without raising the middle edge from its plate. It is very convenient to have a stop for the scales as well as one for the beam. New balances are always so provided. The usual device for stopping the scales consists of two supports immediately below them, which slide up and down, and are furnished with crossed silk ribands or camel's hair brushes. The supports must move with such perfect steadiness, that the scales do not shake in the least upon the removal of the supports from beneath them (provided, of course, the operation be effected with some degree of delicacy and caution). This arrangement, besides facilitating the loading of the scales, affords this advantage—that it enables the operator to put an immediate stop to all trembling or shaking of the scales, and also the convenience that, in cases where one and the same body has to be weighed repeatedly, the weights may be left on the scale without risk to the balance. Single stops fixing both beam and scales by one and the same act (by a turn), appear to me less practical, as the fixing of the scales upon every fresh addition of a small weight, whilst answering no rational purpose, impairs the rapidity of weighing. It is highly advisable to have the case of the balance so arranged that the contrivances for lifting the beam and fixing the scales can be worked while the case remains closed, and consequently from without.

4. It is necessary that the balance should be provided with an index or pointer to mark its oscillations on a graduated arc; this index is more appropriately placed beneath the axis than at the side of the balance.

5. The balance must be provided with a pendulum, or with a spirit level, to enable the operator to place the three edges on an exactly horizontal level; it is best also for this purpose that the case should rest upon three screws.

6. It is very desirable that the beam should have a decimal graduation, so as to enable the operator to weigh the milligramme and its fractions with a centigramme "rider" (Fig. 2). Most modern balances are so constructed that the position of the rider on the beam may be shifted at pleasure, and without opening the glass case, by means of a movable arm which passes through the side of the case.*

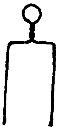

Fig. 2.

7. The balance must be provided with a screw to regulate the centre of gravity, and likewise with two screws to regulate the equality of the arms, and finally with screws to restore instantly the equilibrium of the scales, should this have been disturbed.

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* **Hempel** has a very complete arrangement for placing the small weights and shifting the rider, see Zeitschr. f. anal. Chem. 4, 83. I have, however, no personal experience of its working.

7.

The following experiments serve to test the accuracy and sensibility of a balance.

1. The balance is, in the first place, accurately adjusted, if necessary, either by the regulating screws, or by means of tinfoil, and a milligramme weight is then placed in one of the scales. A good and practically useful balance must turn very distinctly with this weight; a delicate chemical balance should indicate the $\frac{1}{10}$ of a milligramme with perfect distinctness. It should be noted here, that the mere pointing of the index to zero is not sufficient evidence of equilibrium. It is much better to observe the oscillations of the pointer, which if necessary can be brought about by a movement of the hand near one of the scales so as to cause a slight wind. The pointer should traverse very nearly the same space on each side of the zero, less and less with each oscillation, and finally come to rest at zero.

2. Both scales are loaded with the maximum weight the construction of the balance will admit of. The balance is then accurately adjusted, and a milligramme added to the weight in the one scale. This ought to cause the balance to turn to about the same extent as in 1. In most balances, however, it shows somewhat less. It follows from § 5 β that the balance will oscillate more slowly in this than in the first experiment.

3. The balance is accurately adjusted (should it be necessary to establish a perfect equilibrium between the scales by loading the one with a minute portion of tinfoil, this tinfoil must be left remaining upon the scale during the experiment); both scales are then equally loaded, say with fifty grammes each, and, if necessary, the balance is again adjusted (by the addition of small weights). The load of the two scales is then interchanged, so as to transfer that of the right scale to the left, and *vice versâ*. A balance with perfectly equal arms must maintain its absolute equilibrium.

4. The balance is accurately adjusted; it is then arrested and again set in motion; the same process should be repeated several times. A good balance must invariably reassume its original equilibrium. A balance the end edges of which afford too much play to the hook resting upon them, so as to allow the latter slightly to alter its position, will show perceptible differences in different trials. This fault, however, is possible only with balances of defective construction.*

A balance must stand the first, second, and last of these tests. A slight inequality of the arms is of no great consequence, as the error that it would occasion may be completely prevented by the manner of weighing.

As the sensibility of a balance will speedily decrease if the steel edges are allowed to get rusty, delicate balances should never be kept in the laboratory, but always in a separate room. It is also advisable to place within the case a vessel half filled with calcined carbonate of potassa, to keep the air dry. I think I need hardly add that this salt must be recalcined as soon as it gets moist.

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* G. Westphal, mechanician of Celle, has described a mode of construction which excludes the possibility of this fault. (Zeitschr. f. anal. Chem. 7, 294.)

§ 8.

b. The Weights.

Intrinsically it is quite unimportant what unit of weight is adopted. However, most chemists use the gramme on account of its convenience for entering in the book and calculating. With regard to the set of weights, it is generally a matter of indifference for scientific purposes whether the gramme, its multiples and fractions, are actually normal weights or not;* but it is absolutely necessary that they should agree perfectly among themselves—*i.e.*, the centigramme weight must be exactly the one hundredth part of the gramme weight of the set, &c. &c.

Before I describe the testing of the weights, I must call attention to the following points.

1. A set of weights ranging from fifty grammes to one milligramme is fully sufficient for most purposes.

2. The weights should be kept in a well-closing box; and it is desirable likewise that a distinct compartment be appropriated to every one even of the smaller weights.

3. As to the shape best adapted for weights, I think that of short frusta of cones inverted, with a handle at the top, the most convenient and practical form for the large weights. Square pieces of foil, turned up at one corner, are best adapted for the small weights; the foil used for this purpose should not be too thin, and the compartments should be large enough, or else the smaller weights will soon get crinkled and defaced. Each weight (with the exception of the milligrammes) should be distinctly marked.

4. With respect to the material most suitable for the manufacture of weights, I think that, although rock crystal is admirably adapted for normal weights, it is unsuited for the ordinary weights, as their form would be inconvenient, and their price too high. Platinum weights would be sure to be universally adopted, were the metal not too expensive; but as it is, we commonly rest satisfied with having the smaller weights only, from 1 or ·5 gramme downwards, made of platinum foil, using brass weights for all the higher denominations. Brass weights must be carefully shielded from the contact of acid or other vapors, or their correctness will be impaired; nor should they ever be touched with the fingers, but always with small pincers. But it is an erroneous notion to suppose that weights slightly tarnished are unfit for use. It is, indeed, hardly possible to prevent weights for any length of time from getting slightly tarnished. I have carefully examined many weights of this description, and have found them to correspond with one another as exactly as at first. The tarnishing coat is so extremely thin, that even a very delicate balance will generally fail to point out any perceptible difference in the weight. It will, however, be found very advantageous to gild the brass weights previously to the final adjustment.

The following is the only proper way of *testing the weights*, to see whether they agree among themselves:—

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* Still it would be desirable that the makers of analytical weights should endeavor to procure normal weights. It is very inconvenient, in many cases, to find notable differences between weights of the same denomination, but coming from different makers; as I myself have often had occasion to discover.

One scale of a delicate balance is loaded with a one-gramme weight, and the balance is then completely equipoised with small pieces of brass, and finally tinfoil (not paper, since this absorbs moisture). The weight is then removed, and replaced successively by the other gramme weights, and afterwards by the same amount of weight in pieces of lower denominations. The balance is carefully scrutinized each time, and any deviation from the exact equilibrium marked. In the same way it is seen whether the two-gramme piece weighs the same as two single grammes, the five-gramme piece the same as three single grammes and the two-gramme piece, &c. In the comparison of the smaller weights thus among themselves, they must not show the least difference on a balance turning with $\frac{1}{10}$ milligramme. In comparing the larger weights with all the small ones, differences of $\frac{1}{10}$ to $\frac{2}{10}$ milligramme may be passed over. If you wish them to be more accurate, you must adjust them yourself. Experience has taught me that it is invariably the safest way to test every weight one purchases, no matter how high the reputation of the maker may stand. In the purchase of weights chemists ought always to bear in mind that an accurate weight is truly valuable, whilst an inaccurate one is absolutely worthless.*

§ 9.

c. THE PROCESS OF WEIGHING.

We have two different methods of determining the weight of substances; the one might be termed *direct weighing*, the other is called *weighing by substitution.*

In *direct weighing* the substance is placed upon one scale, and the weight upon the other. If the arms of the balance are of equal length, and the scales in a perfect state of equilibrium, it is indifferent upon which scale the substance is placed in the several weighings required during an analytical process; *i.e.*, we may weigh upon the right or upon the left side, and change sides at pleasure, without endangering the accuracy of our results. But if, on the contrary, the arms of our balance are not perfectly equal, or if the scales are not in perfect equilibrium, we are compelled to weigh invariably upon the same scale, otherwise the correctness of our results will be more or less impaired.

Suppose we want to weigh one gramme of a substance, and to divide this amount subsequently into two equal parts. Let us assume our balance to be in a state of perfect equilibrium, but with unequal arms, the left being 99 millimetres, the right 100 millimetres long; we place a gramme weight upon the left scale, and against this, on the right scale, as much of the substance to be weighed as will restore the equilibrium of the balance.

According to the axiom, "masses are in equilibrium upon a lever, if the products of their weights into their distances from the fulcrum are equal," we have consequently upon the right scale ·99 grm. of substance, since $99 \times 1 = 100 \times \cdot 99$. If we now, for the purpose of weighing one-half the quantity, remove the gramme weight from the left scale, substituting a ·5 grm. weight for it, and then take off part of the substance from the right scale, until the balance recovers its equilibrium, there will remain ·495 grm.; and this is exactly the amount we have removed from the scale; we have consequently accomplished our object with respect to the relative weight; and, as we have already remarked, the absolute weight is not generally of so much importance in scientific work. But if we attempted to halve the substance which we have on the right scale, by first removing both the weight and the substance from the scales, and placing subsequently a ·5 grm. weight upon the right scale, and part of the substance upon the left, until the balance recovers its equilibrium, we should have ·505 of substance upon the left scale, since $100 \times \cdot 5 = 99 \times \cdot 505$; and consequently, instead of exact halves, we should have one part of the substance amounting to ·505, the other only to ·485.

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* **Compare Crookes (Chem. News, 15, 191) and K. L. Bauer (Zeitschr. f. anal. Chem. 8, 390).**

If the arms of a balance are equal, but the scales are not in a state of equilibrium, we are obliged to weigh our substances in vessels (see § 10, 6), to ensure accurate results. It is self evident that the weights in this case must likewise be invariably placed upon one and the same scale, and that the difference between the two scales must not vary during the course of a series of experiments.

From these remarks result the two following rules :—

1. It is, under all circumstances, advisable to place the substance invariably upon one and the same scale—most conveniently upon the left.
2. If the operator possesses a balance for his own private and exclusive use, there is no need that he should adjust it at every weighing; but if the balance be used in common by several persons, it is absolutely necessary to ascertain each time whether its state of equilibrium may not have been disturbed.

Weighing by substitution yields not only relatively, but also absolutely accurate results; no matter whether the arms of the balance be of exactly equal lengths or not, or whether the scales be in perfect equipoise or not.

The process is conducted as follows: the material to be weighed—say a platinum crucible—is placed upon one scale, and the other scale is accurately counterpoised against it. The platinum crucible is then removed, and weights substituted for it till equilibrium is restored. It is obvious that the substituted weights will invariably express the real weight of the crucible with absolute accuracy. We weigh by substitution whenever we require the greatest possible accuracy; as, for instance, in the determination of atomic weights. The process may be materially shortened by first placing a tare (which must of course be heavier than the substance to be weighed) upon one scale, say the left, and loading the other scale with weights until equilibrium is produced. This tare is always retained on the left scale. The weights after being noted are removed. The substance is placed on the right scale, together with the smaller weights requisite to restore the equilibrium of the balance. The sum of the weights added is then subtracted from the noted weight of the counterpoise : the remainder will at once indicate the absolute weight of the substance. Let us suppose, for instance, we have on the left scale a tare requiring a weight of fifty grammes to counterpoise it. We place a platinum crucible on the right scale, and find that it requires an addition of weight to the extent of 10 grammes to counterpoise the tare on the left. Accordingly, the crucible weighs 50 *minus* 10 = 40 grammes.

§ 10.

The following *rules* will be found useful in performing the process of weighing :—

1. The balance is to be kept in a dry room, protected from acid fumes, &c., and if possible not exposed to the sun ; it must stand firmly and in a level position. It should not be near a fireplace or stove, otherwise it may be unequally warmed.

2. In ascertaining the weight of a substance, it saves time to try the weights in a strictly systematic way. Suppose, for instance, we want the weight of a crucible, which subsequently turns out to be 6·627 grammes ; well, we place 10 grammes on the other scale, and we find this is too much ; we place the weight next in succession, *i.e.*, 5 grammes, and find this too little ; next 7, too much ; 6, too little ; 6·5, too little ; 6·7, too much ; 6·6, too little ; 6·65, too much ; 6·62, too little ; 6·63, too much ; 6·625, too little ; 6·627, right. I have selected here, for the sake of illustration, a most complicated case ; but I can assure the student that this systematic way of laying on the weights will in most instances lead to the desired end, in half the time required when weights are tried at random. After a little practice a few minutes will suffice to ascertain the weight of a substance to $\frac{1}{10}$ milligramme, provided the balance does not oscillate too slowly.

3. The milligrammes and fractions of milligrammes are determined by a centigramme rider (to be placed on or between the divisions on the beam) far more conveniently than by the use of the weights themselves, and at the same time with equal accuracy. (Comp. § 6, 6.)

4. Particular care and attention should be bestowed on entering the weights in the book. The best way is to write down the weights first by inference from the blanks, or gaps in the box, and to control the entry subsequently by removing the weights from the scale, and replacing them in their respective compartments in the box. The student should from the commencement make it a rule to enter the number to be deducted in the lower line ; thus, in the upper line, the weight of the crucible + the substance ; in the lower line, the weight of the crucible.

5. The balance ought to be arrested every time any change is contemplated, such as removing weights, substituting one weight for another, &c., or it will soon get spoiled.

6. Substances (except, perhaps, pieces of metal, or some other bodies of the kind) must never be placed directly upon the scale, but ought to be weighed in appropriate vessels of platinum, silver, glass, porcelain, &c., never on paper or card, since these, being liable to attract moisture, are apt to alter in weight. The most common method of weighing off a substance is to weigh in the first instance the vessel by itself, and to introduce subsequently the substance into it ; to weigh again, and subtract the former weight from the latter. In many instances, and more especially where several portions of the same substance are to be weighed, the united weight of the vessel and of its contents is first ascertained ; a portion of the contents is then shaken out, and the vessel weighed again ; the loss of weight expresses the amount of the portion taken out of the vessel.

7. Substances liable to attract moisture from the air, must be weighed invariably in closed vessels (in covered crucibles, for instance,

or between two watch-glasses, or in a closed glass tube); fluids are to be weighed in small bottles closed with glass stoppers.

8. A vessel ought never to be weighed whilst warm, since it will in that case invariably weigh lighter than it really is. This is owing to two circumstances. In the first place, every body condenses upon its surface a certain amount of air and moisture, the quantity of which depends upon the temperature and hygroscopic state of the air, and likewise on its own temperature. Now suppose a crucible has been weighed cold at the commencement of the operation, and is subsequently weighed again whilst hot, together with the substance it contains, and the weight of which we wish to determine. If we subtract for this purpose the weight of the cold crucible, ascertained in the former instance, from the weight found in the latter, we shall subtract too much, and consequently we shall set down less than the real weight for the substance. In the second place, bodies at a high temperature are constantly communicating heat to the air immediately around them; the heated air expands and ascends, and the denser and colder air, flowing towards the space which the former leaves, produces a current which tends to raise the scale, making it thus appear lighter than it really is.

9. If we suspend from the end edges of a correct balance respectively 10 grammes of platinum and 10 grammes of glass, by wires of equal weight, the balance will assume a state of equilibrium; but if we subsequently immerse the platinum and glass completely in water this equilibrium will at once cease, owing to the different volume of the two substances; since, as is well known, substances immersed in water lose of their weight a quantity equal to the weight of their own bulk of water. If this be borne in mind, it must be obvious to every one that weighing in the air is likewise defective, inasmuch as the bulk of the substance weighed is not the same with that of the weight. This defect, however, is so very insignificant, owing to the trifling specific gravity of the air in proportion to that of solid substances, that we may generally disregard it altogether in analytical experiments. In cases, however, where absolutely accurate results are required, the bulk both of the substance examined, and of the weight, must be taken into account, and the weight of the corresponding volume of air added respectively to that of the substance and of the weight, making thus the process equivalent to weighing in vacuo.

§ 11.

2. MEASURING.

The process of measuring is confined in analytical researches mostly to gases and fluids. The method of measuring gases has been brought to such perfection by **BUNSEN**, by **REGNAULT** and **REISET**, by **FRANKLAND** and **WARD**, by **WILLIAMSON** and **RUSSELL**, and by others, that it may be said to equal in accuracy the method of weighing. However, such accurate measurements demand an expenditure of time and care, which can be bestowed only on the nicest and most delicate scientific investigations.*

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* A detailed description of **BUNSEN**'s method is to be found in Handwörterbuch der Chemie, by **LIEBIG**, **POGGENDORFF** and **WÖHLER**, 2, 1053 (art. Eudiometer, by

The measuring of fluids in analytical work was resorted to first by DECROIZILLES (*Alkalimeter*, 1806). GAY-LUSSAC materially improved the process, and indeed brought it to the highest degree of perfection (in measuring the solution of chloride of sodium in the wet assay of silver). More recently MOHR* has bestowed much care and ingenuity upon the production of appropriate and convenient measuring apparatus, and has added to our store the eminently practical burette which is known by his name. Still, however much the method of measuring fluids has been perfected, it can never be expected to attain the accuracy of weighing. But, as the inaccuracies inherent in the method may, in most cases, be reduced to the most harmless proportions by appropriate dilution of the fluid to be measured, the process is now resorted to even in most accurate scientific investigations; since it requires much less time than the process of weighing.

The accuracy of all measurings depends upon the measuring vessels, and also upon the way in which the process is conducted.

§ 12.

a. THE MEASURING OF GASES.

We use for the measuring of gases graduated tubes of greater or less capacity, made of strong glass, and sealed off round at one end. The following tubes will be found sufficient for all the processes of gas measuring required in organic elementary analyses, and in the analysis of atmospheric air.

1. A bell-glass capable of holding from 150 to 250 c.c., and about 4 cm. in diameter; divided into c.c.
2. Five or six glass tubes, 12 to 15 mm. bore, and capable of holding from 30 to 40 c.c. each, divided into $\frac{1}{5}$ c.c.

The sides of these tubes should be pretty thick, otherwise they will be liable to break, especially when used to measure over mercury. The sides of the bell-glass should be about 3, of the tubes about 2 mm. thick.

The most important point, however, in connection with measuring instruments is that they be correctly graduated, since upon this of course depends the accuracy of the results. For the method of graduating I refer to BERZELIUS's *Lehrbuch der Chemie*, 4 Aufl. Bd. 10, article *Messen*; also to GREVILLE WILLIAMS's *Chemical Manipulation*.

In testing the measuring tubes we have to consider three things.

KOLBE), and 1, 2 ed., 930 (art. Analyse, volumetrische, fur Gase, by KOLBE and FRANKLAND). I would also refer the student of this branch to the very valuable monograph by BUNSEN (Gasometry, translated by ROSCOE, London, 1857). The methods of measuring gas employed by REGNAULT and REISET, and also by FRANKLAND and WARD, differ from the ordinary method improved by BUNSEN in the following essential particular: in the former case the measuring tubes stand in cylinders filled with water, by which means the temperature of the gas is in a few minutes brought to that of the water, and the time required for a gas analysis is consequently much shortened. With FRANKLAND and WARD's apparatus the measuring of the gas is also independent of the pressure of the atmosphere. Both methods, as a matter of course, require complicated and costly apparatus. These are figured and described minutely in the above-mentioned article by FRANKLAND in the Handwörterbuch. For WILLIAMSON's and RUSSELL's apparatus see Jour. Chem. Soc. 17, 238; and for RUSSELL's modification, *Ib.* (2), 6, 128.

* Lehrbuch der Titrirmethode, by Dr. F. MOHR.

1. Do the divisions of a tube correspond with each other?

2. Do the divisions of each tube correspond with those of the other tubes?

3. Do the volumes expressed by the graduation lines correspond with the weights used by the analyst?

These three questions are answered by the following experiments:

a. The tube which it is intended to examine is placed in a perpendicular position, and filled gradually with accurately measured small quantities of mercury, care being taken to ascertain with the utmost precision whether the graduation of the tube is proportionate to the equal volumes of mercury poured in. For the method of reading off the degrees, see below. The measuring off of the mercury is effected by means of a small glass tube, sealed at one end, and ground perfectly even and smooth at the other. This tube is filled to overflowing by immersion under mercury, care being taken to allow no air bubbles to remain in it; the excess of mercury is then removed by pressing a small glass plate down on the smooth edge of the tube.*

b. Different quantities of mercury are successively measured off in one of the smaller tubes, and then transferred to the other tubes. The same volume of mercury should fill each tube up to the same degree.

Such tubes as are intended simply to determine the relative volume of different gases, need only pass these two experiments; but in cases where we want to calculate the weight of a gas from its volume, it is necessary also to obtain an answer to the third question. For this purpose—

c. One of the tubes is accurately weighed and then filled with distilled water at 17°·5 to the last mark of the scale; the weight of the water is then accurately determined. If the tube agrees with the weights, every 100 c.c. of water at 17°·5 must weigh 99·78 grm.† But should it not agree, no matter whether the error lie in the graduation of the tube or in the adjustment of the weights, we must apply a correction to the volume observed before calculating the weight of a gas therefrom. Let us suppose, for instance, that we find 100 c.c. to weigh 100 grm.: assuming our weights to be correct, the c.c. of our scale are accordingly too large; and to convert 100 of these c.c. into normal c.c. we say:—

$$99{\cdot}78 : 100 :: 100 : x.$$

In gas analysis proper by Bunsen's methods (which are the simplest and most accurate) a suitable eudiometer is indispensable. Bunsen's eudiometer (fig. 3) is a glass tube from 500 to 600 mm. long, having a bore of 20 mm., as far as practicable uniform throughout, the glass not above 2 mm. thick. At the upper sealed end two pieces of fine platinum wire are melted into the glass in opposite points; the inner ends of these wires are clinched down close to the side of the glass, approaching each other at the apex of the eudiometer to between 1 and 2 mm.

The tube is graduated into millimetre divisions by means of a very ingeniously constructed divider. The volumes corresponding to the several divisional lines are subsequently determined by measuring into the tube equal volumes of mercury and noted down in a table. This mode of dividing and adjusting measuring tubes is unquestionably the most accurate.

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* As warming the metal is to be carefully avoided in this process, it is advisable not to hold the tube with the hand in immersing it in the mercury, but with a small wooden holder.

† A gramme is the weight of a c.c. of water in vacuo at 4°.

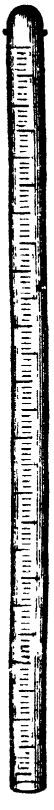

Fig. 3.

Besides this large eudiometer another shorter measuring tube (fig. 4) is required, also graduated into millimetre divisions; it is slightly curved at the lower end. Its length is 250 mm., its bore 20 mm., the thickness of the glass 2 mm.

Bunsen's method of gas analysis requires a laboratory with a northern aspect, of uniform temperature, and takes up much time in consequence of the slow cooling of the gases. In order to adapt it to the use of those who do not possess a suitable laboratory, and to shorten the process, O. **Kersten*** recommends that the eudiometer should be provided with a screw stopper like **Bunsen's** absorption tube, and that the volume should be read off after the immersion of the eudiometer in water. The same result is attained otherwise in J. P. **Cooke's** eudiometer.†

In the measuring of gases we must have regard to the following points:—

1. Correct reading off. 2. The temperature of the gas. 3. The degree of pressure operating upon it. And 4. The circumstance whether it is dry or moist. The three latter points will be readily understood, if it be borne in mind that any alteration in the temperature of a gas, or in the pressure acting upon it, or in the tension of the admixed aqueous vapor, involves likewise a considerable alteration in its volume.

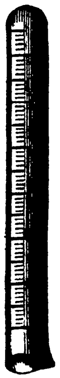

Fig. 4.

§ 13.

1. *Correct reading off.*—This is rather difficult, since mercury in a tube has a convex surface (especially observable with a narrow tube), owing to its own cohesion; whilst water, on the other hand, under the same circumstances has a concave surface, owing to the attraction which the walls of the tube exercise upon it. The tube should invariably be placed in a perpendicular position, and the eye of the operator brought to a level with the surface of the fluid. The first is attained by the help of two plummets suspended at a short distance from the tube, and at a proper distance from each other, or by the aid of any perpendicular door- or window edges that happen to be conveniently situated. The latter is effected by pressing a small mirror firmly against the tube, on the opposite side, and fixing the centre of the eye on the mirror right across the surface of the fluid. When the eye is thus placed in the right position, the mirror is removed, and the height of the fluid read off.

Bunsen generally adopts a different method from this last, using a telescope placed horizontally at a distance of from four to six paces from the eudiometer, and movable in a vertical direction. This arrangement, besides greatly facilitating the reading off, affords, also, in the measuring of gases, this additional great advantage, that, as the observer is placed at a greater distance from the measuring tube, expansion of the gas from his close vicinity to the tube need not be apprehended as in reading off with the aid of the mirror.

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* Zeitschr. f. anal. Chem. 1, 281.

† *Ib.* 7, 86.

In reading off over water, we take the middle of the dark zone formed by the liquid that is drawn up around the inner walls of the tube; in reading off over mercury, we take the middle between the highest point of the surface of the mercury, and the points at which the latter is in actual contact with the walls of the tube. However, the results obtained in this way are only approximate.

Absolutely accurate results cannot be arrived at, in measuring over water or any other fluid that adheres to glass. But over mercury they may be arrived at if the error of the meniscus be determined and the mercury be read off at the highest point. The determination of the error of the meniscus is performed for each tube, once for all, in the following manner: some mercury is poured into the tube, and its height read off on a level with the top of the convex surface; a few drops of solution of chloride of mercury are then poured on the top of the metal; this causes the convexity to disappear; the height of the mercury in the tube is now read off again and the difference noted. In the process of calibrating, the tube stands upright, in that of measuring gases, it is placed upside down; the difference observed must accordingly be doubled, and the sum added to each volume of gas read off.

The mercury intended to serve in the measuring of gases should be pure; it must, more particularly, be as free as possible from lead and tin, which impart to it the property of adhering to glass. Should they be present, they may be removed by keeping the mercury in contact for a day with dilute nitric acid in a shallow basin, taking care to stir

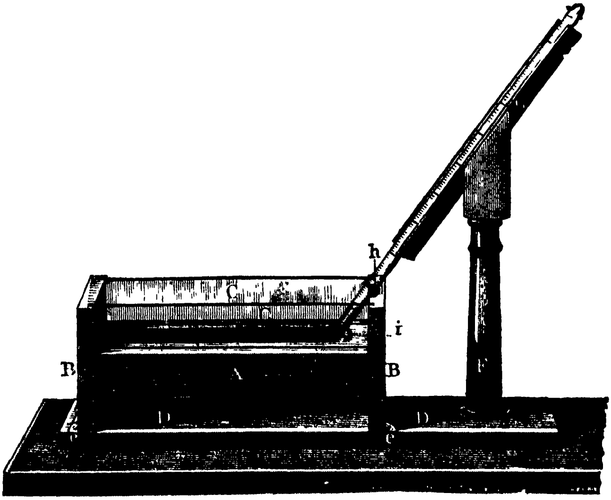

Fig. 5.

frequently. From dust, &c., mercury may be freed by filtration through a cloth.

Bunsen's pneumatic trough (fig. 5) will be found convenient. *A* is a piece of pear-wood 310—350 mm. long, 80—86 mm. broad; the chiselled cavity of the same is 240—250 mm. long, 50 mm. broad and 50 mm. deep. The bottom of the cavity is round, except at one end, where there is a flat surface 32 mm. broad and 50 mm. long. On this a plate of vulcanized caoutchouc 3 mm. thick is cemented. To *A* the two end pieces *BB* are closely joined; they are 19 mm. thick, 100—110 mm. broad, and 150—155 mm. high; they form supports for *A*, and also serve as ends to a further trough, whose sides *CC* consist of strong glass, and fit in grooves in *A* and *BB*. These plates of glass are 310—320 mm. long and 55 mm. high. They are not quite parallel; the lower edges being 67—70 mm. distant from one another, the upper 85 mm. The trough stands on the board *DD*, to which it is fastened by the strips of wood *ee*. A vertical pillar, *F*, screwed into *D*, carries the inclined channel *G*, which is lined with felt, and serves to support the measuring tubes during the passing of gases, &c.; *h* is a round, slanting cut in *B*, serving to receive the tube; *i* is an incision in which the lower end of the measuring tube rests, so that it cannot fall into the lower part of the trough. For use the trough is filled up to an inch of the top of the glass plates, with mercury; 30—35 lb. are necessary. The wooden part of the inside of the trough is rubbed, first moist and then dry, with mercury and solution of chloride of mercury, in order that the metal may adhere to it. To transfer gases which have been collected in large bottles, a similar but larger trough is employed.

Last, to determine accurately the volume of a gas collected over mercury, it is, before all things, necessary that the tube be first filled completely with mercury, to the exclusion of all air bubbles, previous to the introduction of the gas. To this end, the tube, having been rinsed with water, is cleaned and dried with filter paper, with the help of a wooden rod (fig. 6), whose upper end is provided with 10 to 20 little spikes. No filaments must be left behind. The filling with mercury is effected with the aid of the funnel, fig. 7. This should be kept filled with the metal, and its tube, which is provided with a narrow exit, should reach to the bottom of the tube to be filled. The metal thus flowing in from below presents a mirror-like surface on the sides of the glass. If the operator has not such a funnel at his disposal, he may fuse a small funnel to a glass tube drawn out at the lower end.

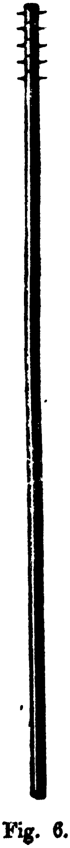
Fig. 6.

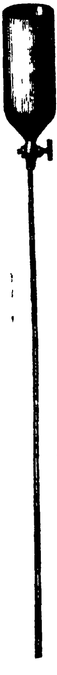
Fig. 7.

§ 14.

2. *Influence of temperature.*—There are two ways of determining the temperature of a gas when measuring it. 1. The temperature of the gas is made to agree with that of the confining fluid, or, in the case of a closed eudiometer, with that of the water in the cylinder provided for the purpose, and then the temperature of the fluid is observed. Or 2. A delicate thermometer is suspended by the side of the gas, and its indication is noted.

If the construction of the apparatus permits the total immersion of the tube in a fluid, uniformity of temperature between the latter and the gas is most readily and speedily obtained ; but if this is not the case, the operator must after every manipulation wait half an hour, or occasionally a whole hour, before he reads off the mercury in the measuring tube and the thermometer.

Proper care must also be taken, after the temperature of the gas has been duly adjusted, to prevent re-expansion during the reading off ; all injurious influences in this respect must accordingly be carefully guarded against, and the operator should, more especially, avoid laying hold of the tube with his hand (in pressing it down, for instance, into the confining fluid) ; making use, instead, of a wooden holder.

As, on account of the necessity of bringing the gas and the surrounding air to the same degree of heat, every sudden change of temperature is prejudicial, it is always advisable to select for the performance of gas analyses a sheltered room with northern aspect.

§ 15.

3. *Influence of pressure.*—If a gas is confined by a fluid, and the level of the latter is the same inside the tube as outside, then the gas is under the actual pressure of the atmosphere ; which may be found at once by inspecting the barometer. But if the confining fluid stands higher inside the tube than outside, the gas is under less pressure,—if lower, it is under greater pressure than that of the atmosphere. In the latter case, the level may always be equalized by raising the tube ; in the former case it may be equalized by depressing the tube, provided the trough is deep enough. When operating over water, the level may in most cases be readily adjusted; when operating over mercury, this is often impossible, more especially with wide tubes.

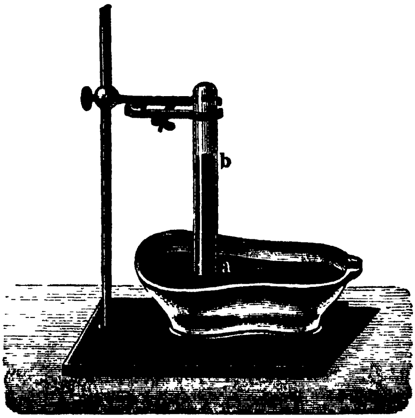

Fig. 8.

In the case illustrated in fig. 8, we have the gas under the pressure of the atmosphere, *minus* the pressure of a column of mercury equal in height to the line *a b*. The pressure may be determined, therefore, by measuring the length of *a b*, and subtracting it from the observed height of the barometer. Suppose, for instance, the barometer stands at 758 mm., and the length of *a b* is = 100 mm., the actual pressure upon the gas will be 758 – 100 = 658 mm. mercury.

If we have water, or some other fluid (solution of potassa, for instance), over the mercury, we proceed generally as if this were not the case ; *i.e.*, we either place the mercury on a level inside and outside the cylinder, or measure the difference between the two surfaces of mercury. The pressure of the column of water, &c., floating over the mercury, is mostly so trifling that it may safely be disregarded. The more correct way, of course, would be to measure the height of the column of water, &c., to reduce this to mercury, and to subtract the result from the actual height of the barometer. But this correction may usually be omitted, since, as has already been stated, absolutely correct measuring is impossible under such circumstances.

§ 16.

4. *Influence of moisture.*—In measuring gases saturated with aqueous vapor, it must be taken into account that the vapor, by virtue of its tension, exerts a pressure upon the confining fluid. The necessary correction is simple, since we know the tension of aqueous vapor for the various degrees of temperature. But before this correction can be applied, it is, of course, necessary that the gas should be actually saturated with the vapor. It is, therefore, indispensable in measuring gases to have the gas saturated with aqueous vapor, or else absolutely dry.

The drying of gases confined over mercury is effected by means of a ball of fused chloride of calcium, stuck on a platinum wire; this is prepared by inserting the wire, bent at the lower end in form of a hook, into a pistol-bullet mould of about 6 mm. inner diameter, and then filling the hollow with chloride of calcium heated just to the fusing point (free from caustic lime). The neck sticking to the ball is, after cooling, removed with a knife. When it is intended to dry a gas, this ball is, with the aid of the wire, pushed through the mercury into the gas; after having been left there for an hour or so, the ball is withdrawn, the gas being now perfectly dry. Whilst the ball remains in contact with the gas, the end of the wire must be kept below the surface of the mercury in the trough, since otherwise we should inevitably have diffusion of the confined gas and the outer air.

Where it can be done, it is more convenient to measure gases in the moist condition. **Bunsen** effects their saturation with moisture by introducing a glass rod with a drop of water the size of a lentil adhering to it, into the empty measuring tube and casting the water off in the top, without wetting any other portion of the tube. The quantity of water thus introduced is more than sufficient, at the common temperature, to saturate with aqueous vapor the gas subsequently passed into the tube.

It is quite obvious from the preceding remarks, that volumes of gases can be compared only if measured at the same temperature, under the same pressure, and in the same hygroscopic state. They are generally reduced to 0°, ·76 metre barometer, and absolute dryness. How this is effected, as well as the manner in which we deduce the weight of gases from their volume, will be found under the Calculation of Analyses.

§ 17.

b. THE MEASURING OF FLUIDS.

In consequence of the vast development which volumetric analysis has of late acquired, the measuring of fluids has become an operation of very frequent occurrence. According to the different objects in view, various kinds of measuring vessels are employed. The number of those that have been proposed has indeed now increased to such an extent, that I must forbear discussing all the forms and arrangements recommended, and simply confine myself to the description of such measuring apparatus as I have found the most practical and convenient in my own laboratory.

Before entering into details, I have to observe that the operator must, in the case of every measuring vessel, carefully distinguish whether it is graduated for holding or for delivering. If you have made use of a vessel of the former description in measuring off 100 c.c. of a fluid, and wish to transfer the fluid completely to another vessel, you must, after emptying your measuring vessel, rinse it, and add the rinsings to the fluid transferred; whereas, if you have made use of a measuring vessel of the latter description, there must be no rinsing.

a. MEASURING VESSELS GRADUATED FOR HOLDING.

aa. Measuring vessels which serve to measure out one definite quantity of fluid.

We use for this purpose—

§ 18.

1. *Measuring Flasks.*

Fig. 9 represents a measuring flask of the most practical and convenient form.

Measuring flasks of various sizes are sold, holding respectively 200, 250, 500, 1000, 2000, &c. c.c. As a general rule, they have no ground-glass stoppers; it is, however, very desirable, in certain cases, to have measuring flasks with ground stoppers. The flasks must be well annealed and of uniform thickness, so that fluids may be heated in them. The line-mark should be placed in the lower third, or at least the lower half, of the neck.

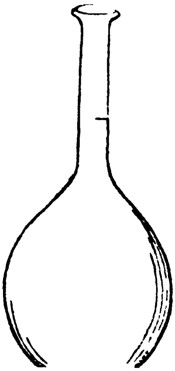

Fig. 9.

Measuring flasks should always be carefully tested. The best and simplest way of effecting this is to proceed thus:—Put the flask, perfectly dry inside and outside, on the one scale of a sufficiently delicate balance, together with a weight of 1000 grm. in the case of a litre flask, 500 grm. in the case of a half-litre flask, &c., restore the equilibrium by placing the requisite quantity of shot and tinfoil on the other scale, then remove the flask and the weight from the balance, put the flask on a perfectly level surface, and pour in distilled water of 17°·5, until the lower border of the dark zone formed by the top of the water around the inner walls corresponds with the line-mark. After having thoroughly dried the neck of the flask above the mark, replace it upon the scale: if this restores the perfect equilibrium of the balance, the water in the flask weighs, in the case of a litre measure, exactly 1000 grm. If the scale bearing the flask sinks, the water in it weighs as much above 1000 grm. as the additional weights amount to which you have to put in the other scale to restore the equilibrium; if it rises, on the other hand, the water weighs as much less as the weights amount to which you have to put in the scale with the flask to effect the same end.

If the water in the litre measure weighs 1000 grm., in the half-litre measure, 500 grm., &c., the measuring flasks are correct. Differences up to ·1 grm. in the litre measure, up to ·07 grm. in the half-litre measure, and up to ·05 grm. in the quarter-litre measure, are not taken into account, as one and the same measuring flask will be found to offer variation to the extent indicated, in repeated consecutive weighings, though filled each time exactly up to the mark with water of the same temperature.

Though a flask should turn out not to hold the exact quantity of water which it is stated to contain, it may yet possibly agree with the other measuring vessels, and may accordingly still be perfectly fit for use for most purposes. Two measuring vessels agree among themselves if the marked numbers of c.c. bear the same proportion to each other as the weights found; thus, for instance, supposing your litre measure to hold 998 grm. water of 17°·5 and your 50 c.c. pipette to deliver 49·9 grm. water of the same temperature, the two measures agree, since

$$1000 : 50 = 998 : 49{\cdot}9.$$

To prepare or correct a measuring flask, tare the dry flask, and then weigh into it, by substitution (§ 9) 1000 grm., or, as the case may be, the half or quarter of that quantity of distilled water of 17°·5. Put the flask on a perfectly horizontal support, place your eye on an exact level with the surface of the water, and mark the lower border of the dark zone by two little dots made on the glass with a point dipped into pitch varnish, or some other substance of the kind. Now pour out the water, place the flask in a convenient position, and cut with a diamond a fine distinct line from one dot to the other.

Measuring flasks are occasionally also graduated for delivering; these, however, can properly be used only in less accurate measurings, since the amount of water remaining in the flask varies not inconsiderably. If you wish to graduate a flask for delivering, or to test one so graduated, pour water into it, empty it again, let it drain for a minute, and then weigh into it the exact weight of distilled water of 17°·5 corresponding to the number of c.c.

As in the above method of testing, the weighings are not conducted at 4°, nor reduced to vacuum, the measuring vessels will not exactly conform to the standard. But if this system is adhered to for all vessels used in measuring fluids, in accordance with F. MOHR's original proposal, they will correspond perfectly among themselves, which is all that is required in volumetric analysis. In the exceptional case of a measuring vessel thus graduated being used in gas analysis, the c.c. may be corrected by multiplying by 1·0022 (F. Mohr*).

bb. Measuring vessels which serve to measure out any quantities of fluid at will.

§ 19.

2. *The Graduated Cylinder.*

This instrument, represented in fig. 10, should be from 2 to 3 cm. wide, of a capacity of 100—300 c.c., and divided into single c.c. It must be ground at the top, that it may be closely covered with a ground-glass plate. The measuring with such cylinders is not quite so accurate as with measuring flasks, as in the latter the volume is read off in a narrower part. The accuracy of measuring cylinders may be tested in the same way as in the case of measuring flasks—viz., by weighing into them water of 17°·5; or, also, very well, by letting definite quantities of fluid flow into the cylinder from a correct pipette or burette, and observing whether or not they are correctly indicated by the scale of the cylinder.

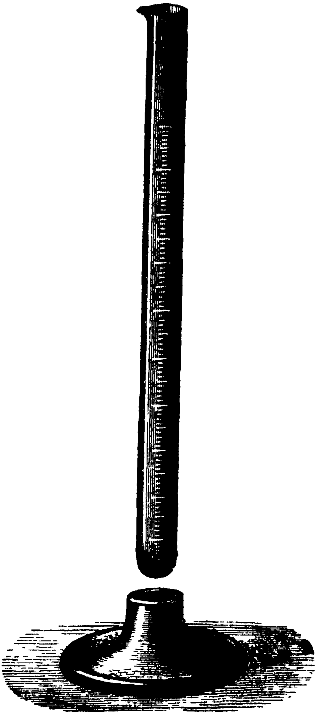

Fig. 10.

β. MEASURING VESSELS GRADUATED FOR DELIVERING.

aa. Measuring vessels which serve to measure out one definite quantity of fluid.

§ 20.

3. *The Graduated Pipette.*

This instrument serves to take out a definite volume of a fluid from one vessel, and to transfer it to another; it must accordingly be of a suitable shape to admit of its being freely inserted into flasks and bottles.

We use pipettes of 1, 5, 10, 20, 50, 100, 150 and 200 c.c. capacity. The proper shape for pipettes up to 20 c.c. capacity is represented in fig. 11; fig. 12 shows the most practical form for larger ones. To fill a pipette suction is applied to the upper aperture, either directly with the lips or through a caoutchouc-tube, until the fluid stands above the mark; the upper orifice (which is somewhat narrowed and ground) is then closed with the first finger of the right hand (the point of which should be a little moist); the outside is then wiped dry, if required, and, the pipette being held in a perfectly vertical direction, the fluid is allowed to drop out, by lifting the finger a little, till it has fallen to the required level; the loose drop is carefully wiped off, and the contents of the pipette are then finally transferred to the other vessel. In this process it is found that the fluid does not run out completely, but that a small portion of it remains adhering to the glass in the point of the pipette; after a time, as this becomes increased by other minute particles of fluid trickling down from the upper part of the tube, a drop gathers at the lower orifice, which may be allowed to fall off from its own weight, or may be made to drop off by a slight shake. If, after this, the point of the pipette be laid against a moist portion of the inner side of the vessel, another minute portion of fluid will trickle out, and, lastly, another trifling droplet or so may be got out by blowing into the pipette. Now, supposing the operator follows no fixed rule in this respect, letting the fluid, for instance, in one operation simply run out, whilst in another operation he lets it drain afterwards, and in a third blows out the last particles of it from the pipette, it is evident that the respective quantities of fluid delivered in the several operations cannot be quite equal. I prefer in all cases the second method—viz., to lay the point of the pipette, whilst draining, finally against a moist portion of the side of the vessel, which I have always found to give the most accurately corresponding measurements.

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* Zeitschr. f. anal. Chem. 7, 287.

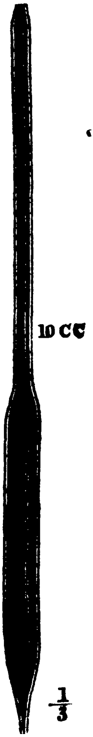

Fig. 11.

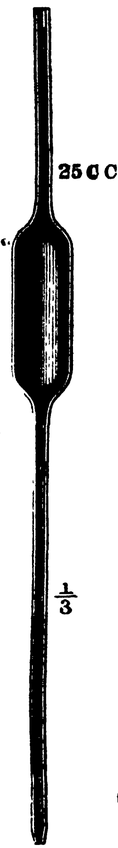

Fig. 12.

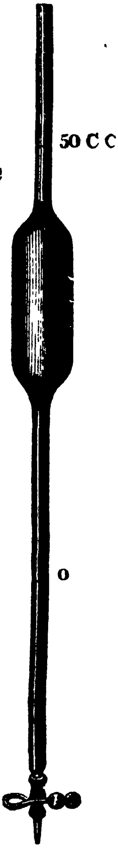

Fig. 13.

The correctness of a pipette is tested by filling it up to the mark with distilled water of 17°·5, letting the water run out, in the manner just stated, into a tared vessel, and weighing; the pipette may be pronounced correct if 100 c.c. of water of 17°·5 weigh 100 grm.

Testing in like manner the accuracy of the measurements made with a simple hand pipette, we find that one and the same pipette will in repeated consecutive weighings of the contents, though filled and emptied each time with the minutest care, show differences up to ·01 grm. for 10 c.c. capacity, up to ·04 grm. for 50 c.c. capacity.

The accuracy of the measurements made with a pipette may be heightened by giving the instrument the form and construction shown in fig. 13, and fixing it to a holder. It will be seen from the drawing that these pipettes are emptied only to a certain mark in the lower tube, and that they are provided with a clip, a contrivance which we shall have occasion to describe in detail when on the subject of burettes. This reduces the differences of measurements with one and the same 50 c.c. pipette to ·005 grm.

Pipettes are used more especially in cases where it is intended to estimate different constituents of a substance in separate portions of the same : for instance, 10 grm. of the substance are dissolved in a 250 c.c. flask, the solution is diluted up to the mark, shaken, and 2, 3, or 4 several portions are then taken out with a 50 c.c. pipette. Each portion consists of $\frac{1}{5}$ of the whole, and accordingly contains 2 grm. of the substance. Of course the pipette and the flask must be in perfect harmony. Whether they are may be ascertained by, for instance, emptying the 50 c.c. pipette 5 times into the 250 c.c. flask, and observing if the lower edge of the dark zone of fluid coincides with the mark. If it does not, you may make a fresh mark, which, no matter whether it is really correct or not, will bring the two instruments in question into conformity with each other.

Cylindrical pipettes, graduated throughout their entire length, may be used also to measure out any given quantities of liquid ; however, these instruments can properly be employed only in processes where minute accuracy is not indispensable, as the limits of error in reading off the divisions are not inconsiderable. For small quantities of liquid this inaccuracy may be avoided, by making the pipettes from tubing of small and uniform bore, and narrowed at both ends. (F. MOHR's measuring pipettes.)

When a fluid runs out of a pipette, drops sometimes remain here and there adhering to the tube ; this arises from a film of fat ; it may be removed by keeping the instrument some time filled with amixture of concentrated solution of bichromate of potassa and sulphuric acid, or with potassa.

bb. Measuring vessels which serve to measure out quantities of fluid at will.

4. *Burettes.*

Of the various forms and dispositions of this instrument, the following appear to me the most convenient :*—

§ 21.

I. *Mohr's Burette.*

This excellent measuring apparatus is represented in fig. 14. It consists of a cylindrical tube, narrower at the lower end for about an inch, with a slight widening, however, at the extreme point, in order that the caoutchouc connector may take a firmer hold. I only use burettes of two sizes, viz., of 30 c.c., divided into $\frac{1}{10}$ c.c. ; and of 50 c.c., divided into $\frac{1}{5}$ c.c. The former I employ principally in scientific, the latter chiefly in technical investigations. The usual length of my 30 c.c. burette is about 50 cm. ; the graduated portion occupies about 43 cm. The bore of the tube is accordingly about 10 mm. ; the upper orifice is, for the convenience of filling, widened in form of a funnel, to 20 mm. ; the width of the lower orifice is 5 mm. For very delicate processes, the length of the graduated portion may be extended to 50 or 52 cm., leaving thus intervals of nearly 2 mm. between the small divisional lines. In my 50 c.c. burettes the graduated portion of the tube is generally 40 cm. long.

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* For other forms of the burette, see F. MOHR, Lehrbuch der Titrirmethode, 3 ed. § 2 ; G. C. WITTSTEIN, Vierteljahresschr. f. prakt. Pharm. 16, 567, and Zeitschr. f. anal. Chem. 7, 84 ; A. GAWALOVSKY, Zeitschr. f. Chem. [N. F.] 6, 129, and Zeitschr. f. anal. Chem. 9, 369 ; GONDOLO, Rev. hebdom. de chim. Nov. 1869, and Zeitschr. f. anal. Chem. 9, 370.

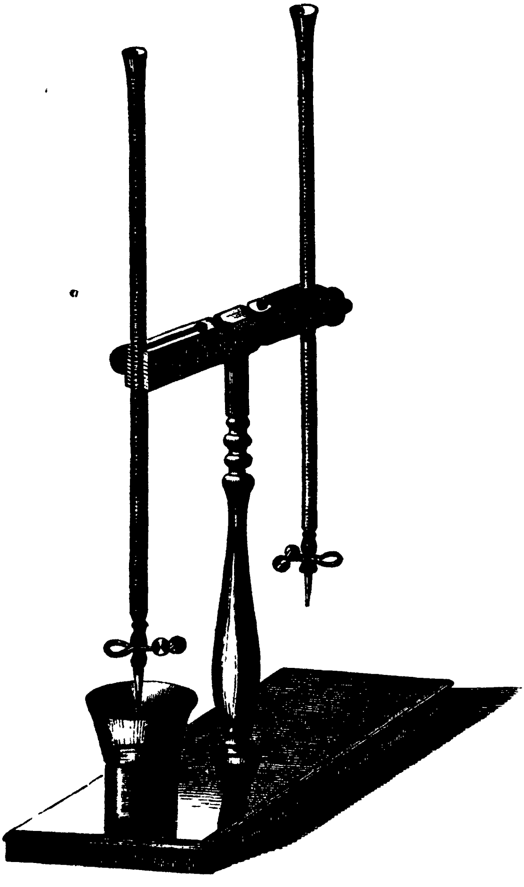

Fig. 14.

To make the instrument ready for use, the narrowed lower end of the tube is warmed a little, and greased with tallow; a caoutchouc tube, about 30 mm. long, and 3 mm. bore, is then drawn over it; into the other end of this is inserted a tube of thick glass, about 40 mm. long, and drawn out to a tolerably fine point; it is advisable to slightly widen the upper end of this tube also, and to cover it with a thin coat of tallow; and also to tie linen-thread round both ends of the connector, to insure perfect tightness.

The space between the lower orifice of the burette and the upper orifice of the small delivery tube should be about 15 mm. The india-rubber tube is now pressed together between the ends of the tubes by the clip. The latter is usually made of brass wire; the form represented in fig. 15 was given by Mohr.

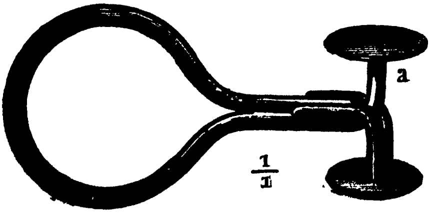

Fig. 15.

A good clip must pinch so tight that not a particle of fluid can make its way through the connector when compressed by it; it must be so constructed that the analyst may work it with perfect facility and exactness, so as to regulate the outflow of the liquid with accuracy.

Mohr* has devised also very practical clips of glass (or horn) and caoutchouc, which I can highly recommend.

Figs. 16 and 17 show the construction of these clips; they are so simple that anybody may easily make them according to Mohr's instructions, which I will give here in his own words:—

"Bend two pieces of flat thermometer tubing from 80 to 90 mm. long, in a very obtuse angle, place between them, in the middle, a piece of cork, about 1½ or 2 mm. thick, and put a caoutchouc ring, cut off from a somewhat wide india-rubber tube, over the part enclosing the cork. Put the caoutchouc tube of the burette between the two glass tubes, press the points together, and push another india-rubber ring over the tubes. These two rings serve to keep the elastic tube of the burette tightly compressed. By pressing on the divergent ends of the glass rods, the elastic bands are stretched asunder, and the liquid drops through the delivery tube; when the pressure on the ends of the tube ceases, the elastic bands, recovering their original tightness, close the connector again."

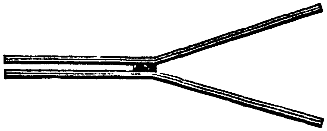

Fig. 16.

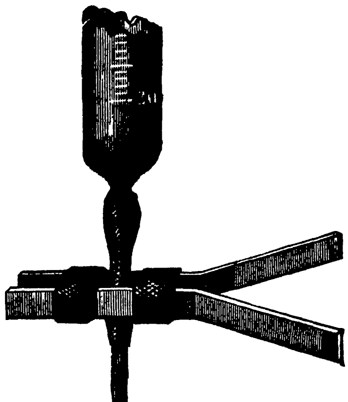

Fig. 17.

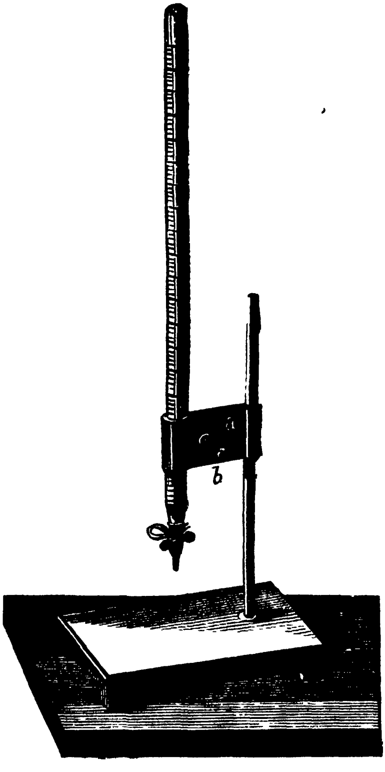

Fig. 18.

For supporting Mohr's burettes, I use the holder represented in fig. 14; this instrument, whilst securely supporting the tube, permits its being moved up and down with perfect freedom, and also its being taken out, without interfering with the clip. The position of the burette must be strictly perpendicular, to insure which, care must be taken to have the grooves of the cork lining, which are intended to receive the tube, perfectly vertical, with the lower board of the stand in a horizontal position. I now have the arm bearing the tubes made movable round the upright, so that first one burette and then the other may be used with ease. A screw (which is wanting in the figure) serves to fix the arm if required. A similar holder, with a brass clamp, is represented in fig. 18.

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* Mohr's Lehrbuch der Titrirmethode.

To charge the burette for a volumetrical operation, fill it a little above the zero, then fully open the clip for a moment so that the fluid may completely fill the point, no air bubble remaining. If an air bubble still remains, bend the point upwards and open the clip again. The bubble may be entirely prevented by filling the lower part of the burette by suction. The burette having, if required, been adjusted in the vertical position, the liquid is allowed to drop out to zero. The instrument is now ready for use. When as much liquid has flowed out as is required to attain the desired object, the analyst, before proceeding to read off the volume used, must wait a few minutes, to give the fluid adhering to the sides time to run down. If the last rule is neglected, the results cannot be expected to agree when, for instance, in one experiment the fluid is run off from the burette in small quantities at a time, and in another experiment the bulk of the fluid required is run off at once, the last drops only being added gradually.

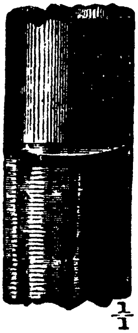

Fig. 19.

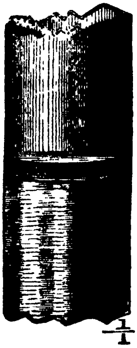

Fig. 20.

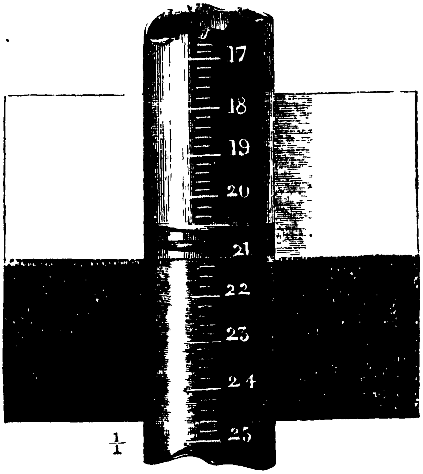

Fig. 21.

The way in which the *reading off* is effected, is a matter of great importance; the first requisite is to bring the eye to a level with the top of the fluid. We must consequently settle the question—What is to be considered the top?

If you hold a burette, partly filled with water, between the eye and a strongly illumined wall, the surface of the fluid presents the appearance shown in fig. 19; if you hold close behind the tube a sheet of white paper, with a strong light falling on it, the surface of the fluid presents the appearance shown in fig. 20. In both cases, you have to read off at the lower border of the dark zone, this being the most distinctly marked line. F. MOHR recommends the following device for reading off:—Paste on a sheet of perfectly white thick paper a broad strip of black paper, and, when reading off, hold this close behind the burette, with the edge of the black paper 2 or 3 mm. below the lower border of the dark zone, as shown in fig. 21; read off at the lower border of the dark zone. Care must be taken to hold the paper invariably in the same position, since, if it be held lower down, the lower border of the black zone will move higher up. I do not myself read off in this manner, but I prefer to read off in a light which causes the appearance represented in fig. 19.

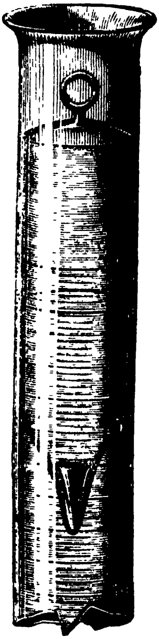

Fig. 22.

By the use of ERDMANN's float* all uncertainties in reading off may be avoided. Fig. 22 represents a burette thus provided. In this case we always read off the degree of the burette which coincides with the circle on the middle of the float. The float must be so fitted to the width of the burette that when placed in the filled burette, it will, on allowing the fluid to run out gradually, sink down with the same without wavering, and when it has been pressed down into the fluid of the closed burette, it will slowly rise again. The weight of the float must, if necessary, be so regulated by mercury that when placed in the filled tube it may cut the fluid with its top uniformly all round. A further important condition of the float is that its axis should coincide as nearly as possible with that of the burette, so that the divisions on the burette may be parallel with the circular line on the float.

The correctness of the graduation of a burette is tested in the most simple way, as follows: fill the instrument with water of 17°·5, then run 10 c.c. into a weighed flask, and weigh; then run another 10 c.c. out, and weigh again, and repeat the operation until the contents of the burette are exhausted. If the instrument is correctly graduated, every 10 c.c. of water of 17°·5 must weigh 10 grm. Differences up to ·01 grm. may be disregarded, since even with the greatest care bestowed on the process of reading off, deviations to that extent will occur in repeated measurements of the uppermost 10 c.c. of one and the same burette. With the float-burettes the weighings agree much more accurately, and the differences for 10 c.c. do not exceed ·002 grm.

MOHR's burette is unquestionably the best and most convenient, and ought to be employed in the measurement of all liquids which are not injuriously affected by contact with caoutchouc. Of the standard solutions used at present in volumetric analysis, that of permanganate of potassa alone cannot bear contact with caoutchouc. For calibrating MOHR's burettes SCHEIBLER gives excellent directions.†

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* Journ. f. prakt. Chem. 71, 194.

† *Ib.* 76, 177.

§ 22.

II. *Gay-Lussac's Burette.*

Fig. 23 represents this instrument in, as I believe, its most practical form.

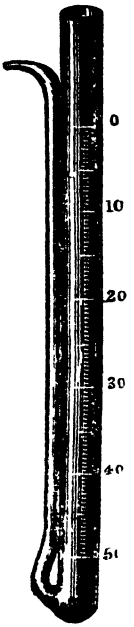

Fig. 23.

I make use of two sizes, one of 50 c.c., divided into ½ c.c., the other of 30 c.c. divided into $\frac{1}{10}$ c.c. The former is about 33 cm. long; the graduated portion occupies about 25 cm.; the bore of the wide tube is 15 mm.; that of the narrow tube 4 mm., which in the upper bent end gradually decreases to 2 mm. The graduated portion of the smaller burette is about 28 cm. long, and has accordingly a bore of about 11 mm.

When operating with a burette of this construction, I hold the instrument with the left hand, letting the bottom lean a little against the chest. By holding the instrument in this way, and occasionally pointing the spout sideways, the operator will be enabled to regulate the outflow of liquid at will. As a general rule, I never let the liquid run back in the narrow tube, in the course of an experiment, since the air bubble enclosed between the fluid in the burette and the drop adhering to the mouth of the spout, makes it generally a task of some difficulty to renew the outflow of the liquid.

The stand which I use to rest my burettes in, consists of a disk of solid wood, from 5 to 6 cm. high, and from 10 to 12 cm. in diameter, with a hole made with the auger and chisel, of proper size to receive the bottom of the burette. This arrangement seems to me more convenient than the method of cementing the burette in a wooden foot.

To overcome the difficulty of renewing the outflow of the liquid, which is always experienced when, during the temporary cessation of the process, air has been enclosed between the liquid in the burette and the drop adhering to the mouth of the spout, MOHR suggests the use of a perforated cork, bearing a short glass tube bent at a right angle. The cork being inserted into the mouth of the wide tube, a piece of caoutchouc is drawn over the short glass tube; by blowing into this with greater or less force, the outflow of the liquid from the spout of the slightly slanting burette may be regulated at pleasure. Instead of blowing with the mouth a caoutchouc balloon may be used. This contains a small round opening by which air enters, and which is closed by the finger during compression. (HERVÉ-MANGON.*)

The reading off of the height of the liquid is effected in the same way as explained in § 21. I prefer, however, placing the burette firmly against a perpendicular partition, either a strongly illumined door, or the pane of a window, to insure the vertical position of the instrument. It is only when operating with rather concentrated, and accordingly opaque solutions of permanganate of potassa, that the method of reading off requires modification; in that case, the upper border of the liquid is noted; and the best way is to place the burette against a white background, and read off by reflected light.

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* Rép. chem. appliquée, 1, 68.

The correctness of the graduation of Gay-Lussac's burettes is tested in the same way as that of Mohr's burettes.

§ 23.

III. *Geissler's Burette.*

In this instrument, which is represented in fig. 24, the narrow tube is placed inside the wide tube instead of outside, as in Gay-Lussac's burette. The part of the inner tube projecting beyond the wide tube is thick in the glass; whilst the part inside, which is of the same bore, is made of very thin glass.

This is a very convenient instrument, and less liable to fracture than Gay-Lussac's burette. I am very fond of working with it.

For the method of reading off and testing the correctness of the instrument, I refer to §§ 21 and 22.

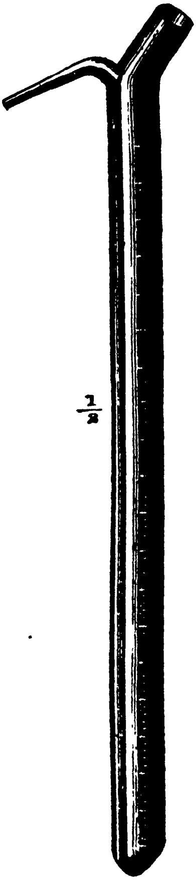


Fig. 24.

II. Preparation of Substances for the Processes of Quantitative Analysis.

§ 24.

1. The Selection of the Sample.

Before the analyst proceeds to make the quantitative analysis of a body, he cannot too carefully consider whether the desired result is fully attained if he simply knows the respective quantity of every individual constituent of that body. This primary point is but too frequently disregarded, and thus false impressions are made, even by the most careful analysis. This remark applies both to scientific and to technical investigations.

Therefore, if you have to determine the constitution of a mineral, take the greatest possible care to remove in the first place every particle of gangue, and disseminated impurities; remove any adherent matter by wiping or washing, then wrap the substance up in a sheet of thick paper, and crush it to pieces on a steel anvil; and pick out with a pair of small pincers the cleanest pieces. Crystalline substances, prepared artificially, ought to be purified by recrystallization; precipitates by thorough washing, &c. In technical investigations—when called upon, for instance, to determine the amount of peroxide present in a manganese ore, or the amount of iron present in an iron ore—the first point for consideration ought to be whether the samples correspond as much as possible to the average quality of the ore. What would it serve, indeed, to the purchaser of a manganese mine to know the amount of peroxide present in a select, possibly particularly rich, sample?

These few observations will suffice to show that no universally applicable and valid rules to guide the analyst in the selection of the sample can be laid down; he must in every individual case, on the one hand, examine the substance carefully, and more particularly also under the microscope, or through a lens; and, on the other hand, keep clearly in view the object of the investigation, and then take his measures accordingly.

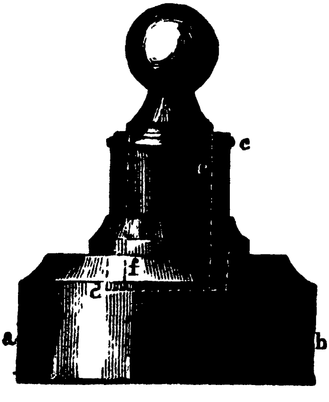
§ 25.

2. Mechanical Division.

In order to prepare a substance for analysis, *i.e.*, to render it accessible to the action of solvents or fluxes, it is generally indispensable, in the first place, to divide it into minute parts, since this will create abundant points of contact for the solvent, and will counteract, and, as far as practicable, remove the adverse influence of the power of cohesion, thus fulfilling all the conditions necessary to effect a complete and speedy solution.

The means employed to attain this object vary according to the nature of the different bodies we have to operate upon. In many cases, simple pounding or triturating is sufficient; in other cases it is necessary to reduce the powder to the very highest degree of fineness, by sifting or elutriation.

The operation of powdering is conducted in mortars; the first and most indispensable condition is, that the material of the mortar be considerably harder than the substance to be pulverized, so as to prevent, as far as practicable, the latter from being contaminated with any particles of the former. Thus, for salts and other substances possessing no very considerable degree of hardness, porcelain mortars may be used, whilst harder substances (including most minerals) require mortars of agate, chalcedony, or flint. In such cases, the larger pieces are first reduced to a coarse powder; this is best effected by wrapping them up in several sheets of writing-paper, and striking them with a hammer upon a steel or iron plate; the coarse powder thus obtained is then pulverized, in small portions at a time, in an agate mortar, until it is reduced to the state of an impalpable powder.



If we have but a small portion of a mineral powder to operate upon, and indeed in all cases where we are desirous of avoiding loss, it is advisable to use a steel mortar (fig. 25) for the preparatory reduction of the mineral to coarse powder. *a b* and *c d* represent the two component parts of the mortar; these may be readily taken asunder. The substance to be crushed (having, if practicable, first been broken into small pieces), is placed in the cylindrical chamber *e f*; the steel cylinder, which fits somewhat loosely into the chamber, serves as pestle. The mortar is placed upon a solid support, and perpendicular blows are repeatedly struck upon the pestle with a hammer until the object in view is attained.

Minerals which are very difficult to pulverize should be strongly ignited, and then suddenly plunged into cold water, and subsequently again ignited. This process is of course applicable only to minerals which lose no essential constituent on ignition, and are perfectly insoluble in water.

In the purchase of agate mortars, especial care ought to be taken that they have no palpable cracks or indentations; very slight cracks, however, that cannot be felt, do not render the mortar useless, although they impair its durability.

Minerals insoluble in acids, and which consequently require fusing, must especially be finely divided, otherwise we cannot calculate upon complete decomposition. This object may be attained either by patiently triturating small portions in an agate mortar, or by levigating, elutriating, or sifting; levigating, or elutriating, however, can be resorted to only in the case of substances which are not attacked by water. Analysts must in future be more cautious on this point, since it has been discovered that many substances which are usually held to be insoluble in water are, in a state of minute division, strongly affected by that solvent; thus, for instance, water, acting upon finely pulverized glass, is found to rapidly dissolve from 2 to 3 per cent. even in the cold (PELOUZE).* Thus, again, finely divided felspar, granite, trachyte and porphyry give up to water both alkali and silica (H. LUDWIG).†

Levigation is effected as follows. Add a little water to the pounded mineral in the mortar, and triturate the paste until all crepitation ceases, or, which is a more expeditious process, transfer the mineral paste from the mortar to an agate or flint slab, and triturate it thereon with a muller. Rinse the paste off, with the washing bottle, into a smooth hemispherical porcelain basin, evaporate the water on the water bath, and mix the residue most carefully with the pestle. (The paste may be dried also in the agate mortar, but at a very gentle heat, since otherwise the mortar might crack.)

To perform the process of *elutriation*, the pasty mass, having first been very finely triturated with water, is washed off into a beaker, and stirred with distilled water; the mixture is then allowed to stand a minute or so, after which the supernatant turbid fluid is poured off into another beaker. The sediment, which contains the coarser parts, is then again levigated, &c., and the operation repeated until the whole quantity is elutriated. The turbid fluid is allowed to stand at rest until the suspended powder has subsided, which generally takes many hours. The water is then finally decanted, and the powder dried in the beaker.

The process of *sifting* is conducted as follows: a piece of fine, well-washed, and thoroughly dry linen is placed over the mouth of a bottle about 10 cm. high, and pressed down a little into the mouth, so as to form a kind of bag; a portion of the finely triturated substance is put into the bag, and a piece of soft leather stretched tightly over the top by way of cover. By drumming with the finger on the leather cover, a shaking motion is imparted to the bag, which makes the finer particles of the powder gradually pass through the linen. The portion remaining in the bag is again triturated in an agate mortar, and, together with a fresh portion of the powder, sifted again; and the same process is continued until the entire mass has passed through the bag into the glass.

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* Compt. Rend. 43, 117-123.

† Archiv der Pharm. 91, 147.

When operating on substances consisting of different compounds it would be a grave error to use for analysis the powder resulting from the first process of elutriation or sifting, since this will contain an undue proportion of the more readily pulverizable constituents. Great care must, therefore, also be taken to avoid loss in the process of elutriation or sifting, as this loss is likely to be distributed unequally among the several constituents. In such cases it is safer, however, to reduce the substance by patiently triturating it dry, and to avoid elutriating or sifting.

Where it is intended to ascertain the average composition of a heterogeneous substance, of an iron ore for instance, a large average sample is selected, and reduced to a coarse powder; the latter is thoroughly intermixed, a portion of it powdered more finely, and mixed uniformly, and finally the quantity required for analysis is reduced to the finest powder. The most convenient instrument for the crushing and coarse pounding of large samples of ore, &c., is a steel anvil and hammer. The anvil in my own laboratory consists of a wood pillar, 85 cm. high and 26 cm. in diameter, into which a steel plate, 3 cm. thick and 20 cm. in diameter, is let to the depth of one-half of its thickness. A brass ring, 5 cm. high, fits round the upper projecting part of the steel plate. The hammer, which is well steeled, has a striking surface of 5 cm. diameter. An anvil and hammer of this kind afford, among others, this advantage, that their steel surfaces admit most readily of cleaning. To convert the coarse powder into a finer, a smooth-turned steel mortar of about 130 mm. upper diameter and 74 mm. deep is used—the final trituration is conducted in an agate mortar.

§ 26.

3. Drying.

Bodies which it is intended to analyze quantitatively, must be, when weighed, in a definite state, in a condition in which they can be always obtained again. Now, the essential constituents of a substance are usually accompanied by an unessential one, viz., a greater or less amount of water, enclosed either within its lamellæ, or adhering to it from the mode of its preparation, or absorbed by it from the atmosphere. It is obvious that before we can weigh out a definite quantity of a substance, we must, in the first place, remove this variable amount of water. *Most solid bodies*, therefore, *require to be dried before they can be quantitatively analysed.*

The operation of drying is of the very highest importance for the correctness of the results; indeed it may safely be averred that many of the differences observed in analytical researches proceed entirely from the fact that substances are analysed in different states of moisture.

Many bodies contain, as is well known, water which is proper to them either as inherent in their constitution or as so-called water of crystallization. In contradistinction to this, we will employ the term *moisture* to designate that variable adherent or mechanically enclosed water, with the removal of which the operation of drying in the sense here in view is alone concerned.

In drying, our object is to remove all moisture, without interfering in the slightest degree with combined water or any other constituent of the body. To accomplish this object, it is requisite that we should know the properties of the substance in the dry state, and whether it loses water or other constituents at a red heat, or at 100°, or in dried air, or even simply in contact with the atmosphere. These data will serve to guide us in the selection of the process of desiccation best suited to each substance. The dried substance should always at once be transferred to a well-closed vessel; glass-tubes, sealed at one end, and of sufficiently thick glass to bear the firm insertion of tight-fitting smooth corks, are usually employed for this purpose. It is advisable to cover the cork with tinfoil.

a. Substances which lose water in contact with the atmosphere; such as sulphate of soda, crystallized carbonate of soda, &c. Substances of this kind turn dull and opaque when exposed to the air, and finally crumble wholly or partially to powder.

They are more difficult to dry than many other bodies. The process best adapted for the purpose, is to press the pulverized salts with some degree of force between thick layers of fine white blotting paper, repeating the operation with fresh paper until the last sheets remain absolutely dry. It is generally advisable in the course of this operation to repowder the salt.

b. Substances which do not yield water to the atmosphere (unless it is perfectly dry), but effloresce in artificially dried air; such as sulphate of magnesia, tartrate of potassa and soda, &c.

Salts of this kind are reduced to powder, which, if it be very moist, is pressed between sheets of blotting paper, as in *a*; after this operation, it must be allowed to remain for some time spread in a thin layer upon a sheet of blotting paper, effectually protected against dust, and shielded from the direct rays of the sun.

§ 27.

c. Substances which undergo no alteration in dried air, but lose water at 100°; tartrate of lime, for instance.

These are finely pulverized; the powder is put in a thin layer into a watch-glass or shallow dish, and the latter placed inside a chamber

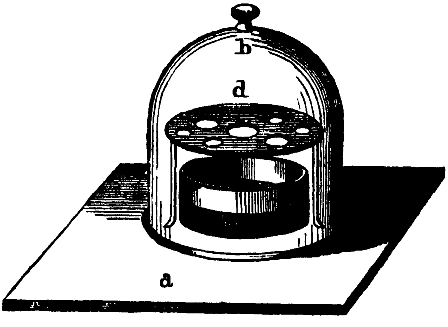

Fig. 26.

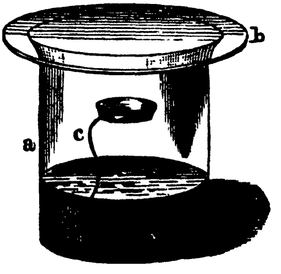

Fig. 27.

in which the air is kept dry by means of sulphuric acid or chloride of calcium. This process is usually conducted in one of the following apparatus, which are termed *desiccators*, and subserve still another purpose besides that of drying, viz., that of allowing hot crucibles, dishes, &c., to cool in dry air.

In fig. 26, *a* represents a glass plate (ground-glass plates answer the purpose best), *b*, a bell jar, with ground rim, which is greased with tallow ; *c* is a glass basin with sulphuric acid ; *d*, a round iron plate, supported on three feet, with circular holes of various sizes, for the reception of the watch glasses, crucibles, &c., containing the substance.

In fig. 27, *a* represents a beaker with ground and greased rim, and filled to one-fourth or one-third with sulphuric acid ; *b* is a ground glass plate ; *c* is a bent wire of lead, which serves to support the watch glass containing the substance.

Fig. 28 is a similarly constructed apparatus containing chloride of calcium.

Fig. 29 represents a readily portable desiccator, used more particularly to receive crucibles in course of cooling, and carry them to the balance. The instrument consists of a box made of strong glass ; the lid must be ground to shut air-tight ; the joint is greased with tallow. The outer diameter is 105 mm. ; the sides are 6 mm. thick. The aperture has a diameter of 80 mm. ; the bottom up to the small part is 65 mm. high ; the lid has the same height ; the small part itself is 15 mm. high, and ground to a slightly conical shape. A brass ring, with rim, fits exactly into the aperture ; the rim must not project beyond the glass. The ring bears a triangle of iron, or, better, platinum wire, intended for the reception of crucibles, &c. The bottom is one-third filled with chloride of calcium.

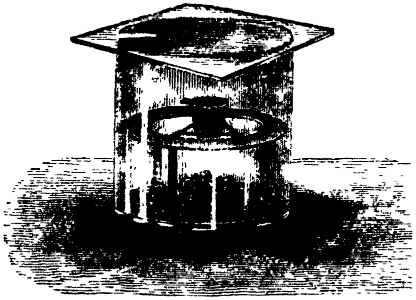

Fig. 28.

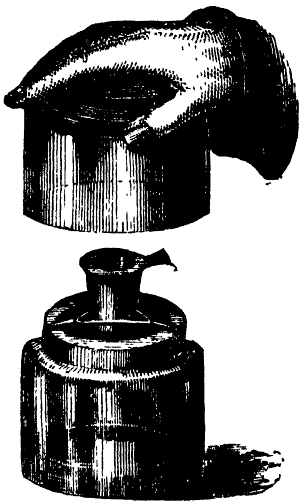

Fig. 29.

Fig. 30 represents the desiccator constructed by A. Schrötter, upon the principle of affording free egress to the air, which expands as soon as hot crucibles are placed inside the apparatus ; the expanding air escapes, in the first place, through the little tube *a*, then through the two lateral apertures in the lower part of *b*; the air-bubbles lastly, which ascend through the sulphuric acid in *c*, make their escape from the bulb *d*, which is filled with chloride of calcium. When the apparatus is cooling, perfectly dry air re-enters by the same way. The operation may be considered at an end when no more air-bubbles ascend through the sulphuric acid. The little tube *e* serves to catch the sulphuric acid that might be carried down through *a*; this tube must not close the lower orifice of the bell-jar air-tight, and the cork holding it must be channelled; *f* serves as a stand for the bell-glass. This desiccator affords the advantage that the substances placed in it are cooled in dry air of the common pressure and have accordingly, when removed from the apparatus, no tendency to attract air (and consequently moisture), which cannot be said of substances cooled in air slightly rarefied by heat. The body which it is intended to dry is kept exposed to the action of the dry air in the glass, until it shows no further diminution of weight. Substances upon which the oxygen of the air exercises a modifying influence are dried in a similar manner, under the exhausted receiver of an air-pump. Substances which, though losing no water in dry air, yet give off ammonia, are dried over quicklime, mixed with some chloride of ammonium in powder, and consequently in any anhydrous ammoniacal atmosphere.

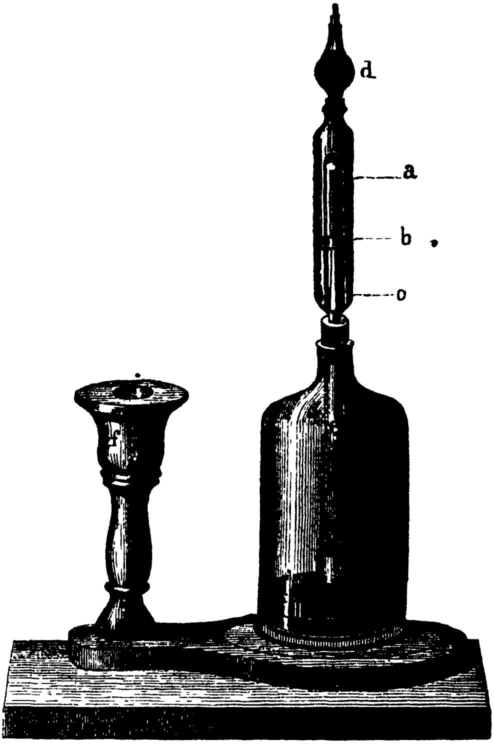

Fig. 30.

§ 28.

d. Substances which at 100° *completely lose their moisture, without suffering any other alteration,* such as bitartrate of potassa, sugar, &c. These are dried in the water-bath; in the case of slow-drying substances, or where it is wished to expedite the operation, with the aid of a current of dry air.

Fig. 31 represents the water-bath most commonly used. It is made either of tinplate, or, better, of sheet copper, and, to adapt it for use also as an oil-bath, soldered with brass. The engraving renders a detailed description unnecessary. The inner chamber, *c*, is surrounded on five sides by the outer case or jacket, *d e*, without communicating with it. The object of the apertures *g* and *h* is to effect change of air, which purpose they answer sufficiently well. When it is intended to use the apparatus, the outer case is filled to about one-half with rain-water, and the aperture *a* is closed with a perforated cork, into which a glass tube is fitted; the aperture *b* is entirely closed. If the apparatus is intended to be heated over a fire, it should have a length of about 20 cm. from *d* to *f*; but if over a gas-, spirit-, or oil-lamp, it should be only about 13 cm. long. In the former case, the inner chamber is 17 cm. deep, 14 broad, and 10 high; in the latter case, it is 10 cm. deep, 9 broad, and 6 high. The temperature in the inner chamber never quite reaches 100°; to bring it up to this point, F. ROCHLEDER has suggested (in a private communication) to close *b* with a double-limbed tube, the outer longer limb of which dips into a cylinder filled with water; *a* is in that case closed with a perforated cork bearing a sufficiently tall funnel tube, which fits air-tight. The lower end of this tube reaches down to one inch from the bottom.

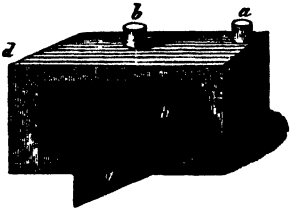

Fig. 31.

In large analytical laboratories water is usually kept boiling all day long, for the production of distilled water. The boilers used in my own laboratory have the shape of somewhat oblong square boxes, about 120 cm. long, 60 broad, and 24 high; the front of the boiler has soldered into it, one above the other, two rows of drying-chambers, or closets, of the kind shown in fig. 31. This gives so many ovens, that almost every student may have one for his special use. Most of these ovens are from 11 to 12 cm. deep and broad, and 8 cm. high; some of them, however, are 16 cm. deep and broad, to enable them to receive large-sized dishes.

The substances to be dried are usually put on double watch-glasses, laid one within the other, which are placed in the oven, and the door is then closed. In the subsequent process of weighing, the upper glass, which contains the substance, is covered with the lower one. The glasses must be quite cold before they are placed on the scale. In cases where we have to deal with hygroscopic substances, the re-absorption of water upon cooling is prevented by the selection of close-fitting glasses, which are held tight together by a clip (fig. 32), and allowed to cool with their contents under a bell-glass over sulphuric acid (see fig. 26). These latter instructions apply equally to the process of drying conducted in other apparatus.

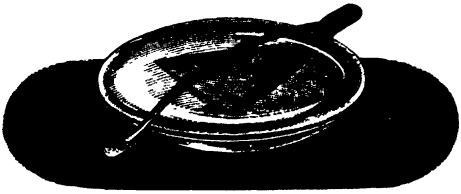

Fig. 32.

The clip used for keeping the watch-glasses pressed together is, in all cases where it is intended to ascertain the loss of weight on drying, to be looked upon as belonging to the glasses, and weighed with them. It is either made of two strips of thin brass, about 10 cm. long and 1 wide, which are soldered together at the ends to the extent of 5 to 6 mm., or it is formed of one piece, as shown in the figure.

The following apparatus serve for drying substances in a current of air:—

In fig. 33 (*A*) the current is caused simply by heating the air, which renders this apparatus very convenient for use. *a b* is a case of sheet copper, or tin plate, into which the canal *c d* is soldered; the latter communicates with the chimney *e f*; this is surrounded on three sides by the cover *g h*, which again communicates with *a b*. The cover has no opening at the top. At *i* is a round aperture leading into the canal, and which may be closed with a cork; *l k* is provided with a well-fitting sliding door running in grooves. When the apparatus is to be used, the aperture *n*, which serves to let off the water, is closed with a cork, the outer case is half filled—through *m*—with water, which is then heated to boiling. The watch-glasses with the substances to be dried are placed on the holes of the sliding shelf *B*, and the latter is introduced into the canal at *l k*, which is then closed. An upward current is soon produced in the chimney, heated as it is, by the steam surrounding it, and the cold air flowing in through *i*, and passing over the drying substances, carries away with it the evaporating moisture. There is a slight disadvantage attending this method—viz., the cold air which passes through keeps the drying substances always a little below 100°; this may be easily remedied, however, by conducting the air, in the first place, through a tube running along under the bottom of the canal (to which it is soldered) from one end to the other and back again. The air is thus heated to 100°, before coming into contact with the drying substance. This tube has been omitted from the figure, to avoid confusion. To render the apparatus still more useful, round holes of different sizes may be cut in the top of the case; these holes, for which proper covers must be provided, serve for the reception of small evaporating dishes. The aperture *m* may, in that case, of course, be omitted. The apparatus is, according to the requirements of the case, made from 20 to 30 cm. long, with a depth of 15, and height of about 10 cm. The chimney should be 6 cm. wide, and 3 high. If it be desirable to create a stronger draught of air than that produced by the little chimney, air which has previously been transmitted through sulphuric acid, or through a chloride of calcium tube, may be blown into *i* by means of a gasometer, or an india-rubber balloon, or some other contrivance. Or air, dried by sulphuric acid, may be drawn through by means of the hydraulic air-pump (§ 47), or an aspirator

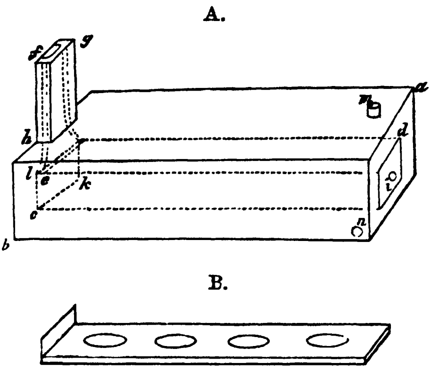

Fig. 33.

(*d* in fig. 34); in this case a round tube should be joined to the little chimney, which may thus be fitted with a cork bearing a glass tube. If a higher temperature than that of boiling water be required, the apparatus (which must then be of copper) is filled with oil, and the temperature determined by a thermometer, fixed in *m* by a cork.

In the apparatus fig. 34, the current of air is produced by an aspirator. *a* represents a flask filled one-third with sulphuric acid; *c* a glass vessel (commonly called a Liebig's drying-tube), and *d* a tin vessel, provided with a stop-cock at *e*. Fig 35 represents a small tin vessel, containing water and covered with a lid; *a* and *b* serve to receive the ascending limbs of *c*. The tube *c* is first weighed with the substance, then placed in the water-bath, fig. 35, which is placed over a spirit- or gas-lamp; the aspirator *d* is then filled with water, and *c* connected with the flask *a* by the perforated cork *g*, and with *d* by means of a caoutchouc tube *f*. If the stop-cock *e* be now opened so as to cause the water to drop from *d*, the air will pass through the tube *b*, and after being dehydrated by the sulphuric acid, will pass over the heated substance in *c*. After the operation has been continued for some time, it is interrupted for the purpose of weighing the tube *c* and its contents, and then resumed again, and continued until the weight of *c* (and its contents) remains constant. If the operator possesses an hydraulic air-pump (§ 47), this may be conveniently substituted for the aspirator. Towards the end of the process a small chloride of calcium tube should be inserted at *f*. As the current of cold air plays upon the substance, the latter never really reaches 100°. It is, therefore, sometimes advisable to substitute for the water in the bath a saturated solution of common salt.

Fig. 34.

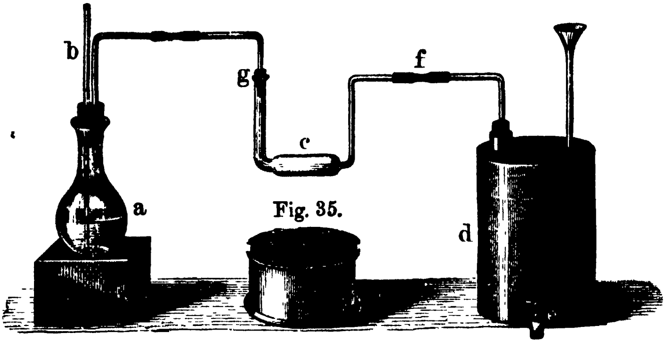

Fig. 35.

With this substitution, the last apparatus will be found to effect its purpose the most expeditiously. It is not adapted, however, for drying such substances as have a tendency to fuse or agglutinate at 100°. This apparatus is to be recommended less for estimations of moisture than for merely drying, as glass is somewhat acted on by long contact with boiling water; and consequently the drying-tube loses weight to a slight extent in the course of the operation. However, different kinds of glass vary in this respect.

§ 29.

e. Substances which persistently retain moisture at 100°, *or become completely dry only after a very long time; but which are decomposed by a red heat.*

The drying of such substances is effected in baths of air, oil, paraffin, or mercury, or on the drying disk (§ 31), at a temperature of 110°, 120°, or still higher, sometimes with the aid of a current of air, sometimes without, sometimes in rarefied air, sometimes in dilute carbonic acid.

Figs. 36 and 37 represent two air-baths of the simplest construction; the former adapted for the simultaneous drying of several substances, the latter more particularly suited for the drying of a single substance.

In fig. 36, *a b* is a case of strong sheet copper, soldered with brass, of a width and depth of 15 to 20 cm., and corresponding height. The aperture *c* receives a perforated cork, into which is fixed a thermometer, *d*, which reaches into the interior of the case; *e* is a wire stand, on which are placed the watch-glasses with the substances to be dried. The case is heated by means of a gas-, spirit-, or oil-lamp. When the temperature has once reached the intended point, it is easy to maintain it pretty constant, by regulating the flame.* In order to limit as much as possible the cooling from without, it is advisable to put over the whole apparatus a pasteboard hood with a movable front.

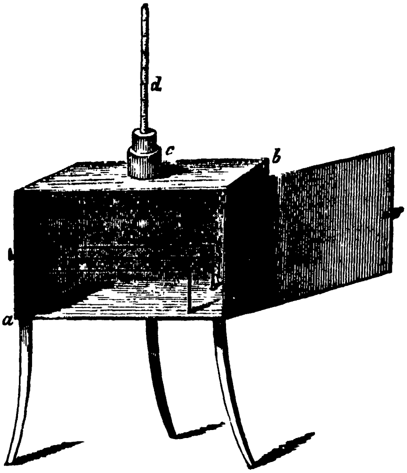

Fig. 36.

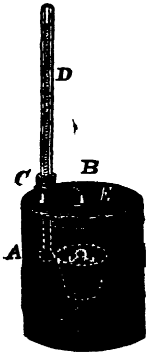

Fig. 37.

In fig. 37, *A* is a box of strong sheet copper, about 11 cm. high, and 9 wide. The box is closed with the loose-fitting cover *B*, which is provided with a narrow rim, and has two apertures, *C* and *E*; *C* is intended to receive the thermometer *D*, which is fitted into it by a perforated cork, *E* affords an exit to the aqueous vapors, and is, according to circumstances, either left open, or loosely closed. In the interior of the box, about half way up, are fixed three pins, supporting a triangle of moderately stout wire, upon which the crucible with the substance is placed uncovered. The bulb of the thermometer approaches the crucible as closely as possible, but without touching the triangle. The heating is effected by means of a gas- or spirit-lamp. When the apparatus has cooled sufficiently to be laid hold of without inconvenience, the lid is removed, the crucible, which is still warm, taken out, covered, and allowed to cool in a desiccator; and weighed when cold.

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* With a gas-lamp, **Kemp's** regulator improved by **Bunsen** (made by **Desaga**, Heidelberg), may advantageously be used to obtain constant temperatures. An alteration in this instrument has been recommended by T. **Schorer** (Zeitschr. f. anal. Chem. 9, 213). **Scheibler's** regulator (*Ib.* 7, 88) is more certain in its action, especially when the pressure of the gas is liable to sudden changes, but, as it depends on an electro-magnet, its construction is more complicated.

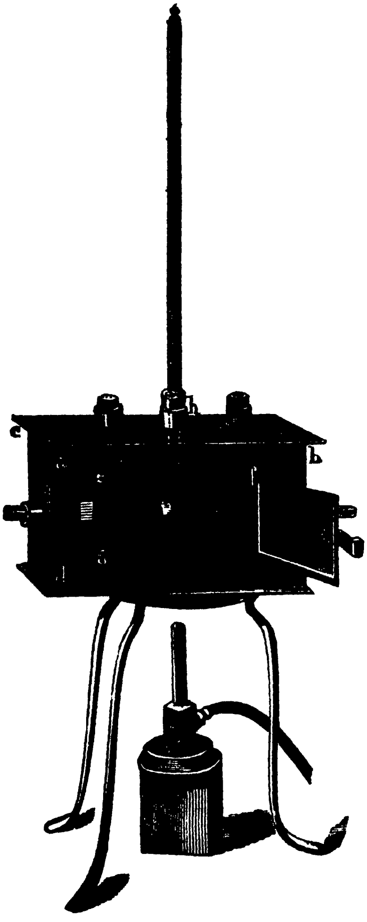

Fig. 38.

The air-bath, fig. 38, serves for the drying of substances in a bulb-tube, with simultaneous application of a current of dry air. The apparatus consists of a box made of sheet iron, of the following dimensions:— $ab = 20$, $ac = 13$, $ad = 12$, $ef = 11$, $eg = 6$ cm. The apertures of both sides have a diameter of 16 mm. The bulb of the thermometer should be on a level with that of the bulb-tube, touching it at the side. To this end, the aperture *h* must not be placed in the middle line, but 1 cm. behind it. It is easy to attain in this apparatus a temperature of from 200 to 260°. To produce the current of dry air, one of the projecting ends of the bulb-tube is connected with the hydraulic air pump (§ 47), or an aspirator, as in fig. 34, the other with a chloride of calcium tube, or wash bottle containing sulphuric acid; the current should be somewhat rapid at first, slower afterwards. If it is intended to weigh the tube with the dried substance, it is allowed to cool, with a current of dry air still continuing to pass through.

In the air-bath, fig. 39, the drying is promoted by alternate exhaustion and re-admission of air. *a* represents a vessel of strong sheet copper, soldered with brass, and provided with two apertures at the top; *b* is a small glass tube, containing the substance; *c* a thermometer; *d* a chloride of calcium tube; *e* an exhausting syringe, for which, of course, a mercurial or an hydraulic air-pump may be substituted. The operation is commenced by heating *a* to the desired degree ; *b* and *d* are then exhausted. After the lapse of a few minutes, fresh air is readmitted through the stop-cock *f*, which, passing over the chloride of calcium in *d*, is completely dried. The same process of alternate exhaustion and readmission of air is repeated until the interior of the tube *g* ceases to exhibit even the faintest trace of moisture, when cooled by the application of wool saturated with ether.

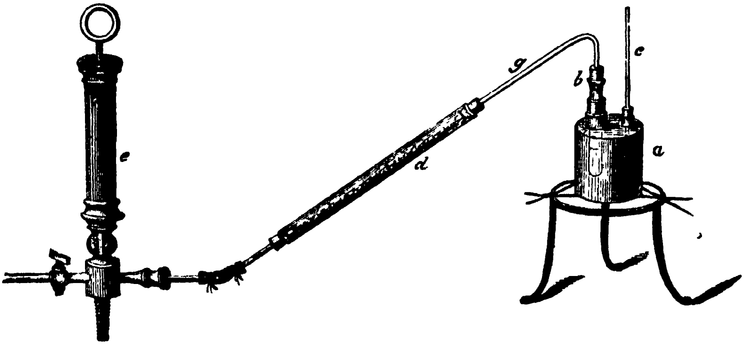

Fig. 39.

§ 30.

The copper apparatus represented in fig. 31 is employed also as an oil-bath ; when used for that purpose, the outer case is filled two-thirds with refined rape-oil. To note the temperature, a thermometer is inserted, by means of a perforated cork, in the aperture *a* ; with the bulb reaching nearly to the bottom, or, at all events, entirely immersed in the oil. As the oil, when heated, emits a most disagreeable smell, I often use paraffin instead. The air-bath represented in fig. 30 will also serve the purpose of an oil-bath. If it is intended to weigh the substance after drying in a tube, a shorter tube is selected for the purpose, which readily admits of insertion into the tube standing in the oil.

Many organic substances, when dried at a somewhat high temperature, suffer alteration by the action of the atmospheric oxygen (F. ROCHLEDER*). In the drying of such substances, oxygen must accordingly be excluded.

Figs. 40 and 41 represent the apparatus devised by ROCHLEDER for this purpose. The former may also be advantageously used for drying in a current of air. In the latter the drying is effected in a rarefied gas. *B* in fig. 40 is a copper plate cylinder, 18 cm. high and 9 cm.

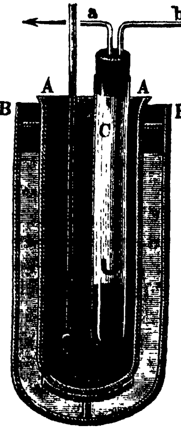

Fig. 40.

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* Journ. f. prakt. Chem. 66, 208.

in diameter, it is filled with oil or paraffin. *A* is fixed in *B*, it is made of iron or glass and contains mercury, in which a thermometer and the tube *C* dip. *C* contains the substance. The dried gas (hydrogen, carbonic acid, air, &c.) enters at *b* and escapes at *a*, if necessary through a chloride of calcium tube. To prevent the current from blowing on to the powdered substance the end of *b* is bent upwards. The advantage of having mercury in *A* is that *C* is not soiled. In fig. 41 the cock *H* is screwed on at *a*, to the air-pump ; *b* is connected, by means of an india-rubber tube, with a caoutchouc-bag (or a bladder), filled with carbonic acid. *B* is an oil-bath ; the temperature of the bath is noted by means of a thermometer ; *S* is a wide-mouthed vessel of strong glass, placed in the bath, which serves to receive the substance to be dried, contained in a glass tube as wide as practicable, and sealed at the bottom. By working the air-pump with the cock *H* open and *H'* closed the air in *S* is rarefied ; by closing *H*, and opening *H'*, the apparatus is filled with carbonic acid, freed from moisture in its passage through the chloride of calcium tube, *C'*. By repeating this operation, the apparatus is filled completely with dry carbonic acid. *H'* is then closed, and the pump set to work. The oil-bath is then heated to the desired degree, carbonic acid being admitted, from time to time, through *H'*. With the carbonic acid pumped out, after closing the cock *H'*, is removed also the moisture absorbed by it, which is retained in the chloride of calcium tube *C*. The entire operation is completed within an hour.

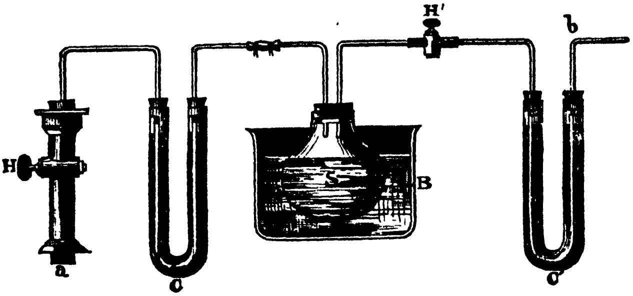

Fig. 41.

§ 31.

In technical and agricultural chemical processes, when it is required to dry a number of samples simultaneously at a rather high temperature, the *drying-disk*, devised by myself, and represented in fig. 42, will be found convenient.

This apparatus consists of a turned cast-iron plate, 37 mm. thick and 21 cm. in diameter ; the weight is about 8 kilogrammes. Owing to the latter circumstance, the heat is very uniformly diffused through its entire mass, and it is easy to maintain it steadily at the desired temperature. The plate has six smooth cylindrical cavities, at equal distances from each other and the centre, in which six turned brass pans, of 55 mm. diameter and 18 mm. height in the clear, are fitted somewhat loosely, to admit of their ready removal after heating. The pans are provided with small handles, turned towards the periphery of the disk, and resting in appropriate grooves. Behind every cavity is stamped on the plate a number, from 1 to 6; the handles of the pans bear corresponding numbers, so that every pan has its own proper cavity. The distance from the centre of the plate to the centre of the pans is 6·5 cm.; the rims of the pans are level with the surface of the plate. Five of the pans are intended to receive the samples (ores, parts of plants, &c.); the sixth receives the thermometer, to which end a brass ring is fitted into it, projecting 3 cm. above the surface. The pan, which is thereby heightened, is filled with brass or copper filings, and the bulb of the thermometer immersed in these down to the bottom. The lamp is placed under the centre of the plate.

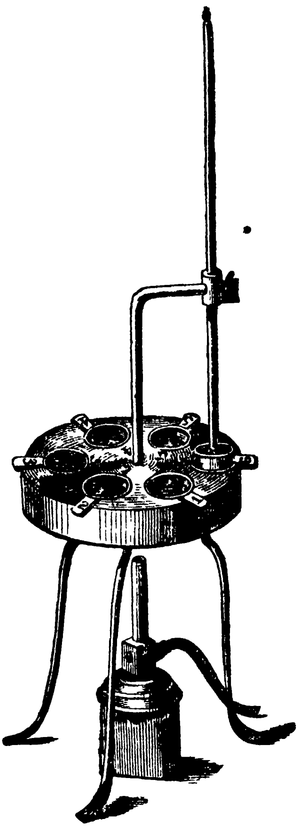
Fig. 42.

f. Substances which suffer no alteration at a red heat, such as sulphate of baryta, pearlash, &c., are very readily freed from moisture. They need simply be heated in a platinum or porcelain crucible over a gas or spirit-lamp until the desired end is attained. The crucible, having first been allowed to cool a little, is put, still hot, in a desiccator, and finally weighed when cold.

III. General Procedure in Quantitative Analysis.

§ 32.

It is important, in the first place, to observe that we embrace in the following general analytical method only the separation and determination of the metals and their combinations with the metalloids, and of the inorganic acids and salts. With respect to other compounds, it is not easy to lay down a universally applicable method, except that their constituents usually require to be converted first into acids or bases, before their separation and estimation can be attempted; this is the case, for instance, with the sulphide of phosphorus, chloride of sulphur, chloride of iodine, sulphide of nitrogen, &c.

The quantitative analysis of a substance presupposes an accurate knowledge of its properties, and of the nature of its constituents. These data will enable the operator at once to decide whether the direct estimation of each constituent is necessary; whether he need operate only on one portion of the substance, or whether it would be advantageous to determine each constituent in different portions. Let us suppose, for instance, we have a mixture of chloride of sodium and anhydrous sulphate of soda, and wish to ascertain the proportion in which these two substances are mixed. Here it would be superfluous to determine each constituent directly, since the determination either of the quantity of the chlorine, or of the sulphuric acid, is quite sufficient to answer the purpose; still the estimation of both the chlorine and the sulphuric acid will afford us an infallible control for the correctness of our analysis; since the united weights of these two substances, added to the sodium and soda respectively equivalent to them, must be equal to the weight of the substance taken.

These estimations may be made, either in one and the same portion of the mixture, by first precipitating the sulphuric acid with nitrate of baryta, and subsequently the hydrochloric acid from the filtrate with nitrate of silver; or a separate portion of the mixture may be appropriated to each of these two operations. Unless there is some objection to its use (*e.g.*, deficiency or heterogeneousness of substance), the latter method is more convenient and generally yields more accurate results; since, in the former method, the unavoidable washing of the first precipitate swells the amount of liquid so considerably that the analysis is thereby delayed, and loss of substance less easily guarded against.

Before beginning all analyses, at least those of a more complex nature, the student should write out an exact plan, and accurately note on paper, during the entire process, everything that he does. It is in the highest degree unwise to rely on the memory in a complicated analysis. When students, who imagine they can do so, come, a week or a fortnight after they have begun their analysis, to work out the results, they find generally too late that they have forgotten much, which now appears to them of importance to know. The intelligent pursuit of chemical analysis consists in the projecting and accurate testing of the plan; acuteness and the power of passing in review all the influential chemical relations must here support each other. He who works without a thoroughly thought-out plan, has no right to say he is practising chemistry; for a mere unthinking stringing together of a series of filtrations, evaporations, ignitions, and weighings, howsoever well these several operations may be performed, is not chemistry.

We will now proceed to describe the various operations constituting the process of quantitative analysis.

§ 33.

1. WEIGHING THE SUBSTANCE.

The amount of matter required for the quantitative analysis of a substance depends upon the nature of its constituents; it is, therefore, impossible to lay down rules for guidance on this point. Half a gramme of chloride of sodium, and even less, is sufficient to effect the estimation of the chlorine. For the quantitative analysis of a mixture of common salt and anhydrous sulphate of soda, 1 gramme will suffice; whereas, in the case of ashes of plants, complex minerals, &c., 3 or 4 grammes, and even more, are required. 1 to 3 grm. can therefore be indicated as the average quantity suitable in most cases. For the estimation of constituents present in very minute proportions only, as, for instance, alkalies in limestones, phosphorus or sulphur in cast-iron, &c., much greater quantities are often required—10, 20, 50, 100, or 200 grammes.

The greater the amount of substance taken the more accurate will be the analysis; the smaller the quantity, the sooner as a rule will the analysis be finished. We would advise the student to endeavour to combine accuracy with economy of time. The less substance he takes to operate upon, the more carefully he ought to weigh; the larger the amount of substance, the less harm can result from slight inaccuracies in weighing. Somewhat large quantities of substance are generally weighed to 1 milligramme; minute quantities, to $\frac{1}{10}$ milligramme.

If *one* portion of a substance is to be weighed off, we first weigh wo watch-glasses which fit on each other, or a platinum crucible with lid, then we put some substance in, and weigh again; the difference between the two weighings gives the weight of he substance taken. This mode of weighing off, however, is only to be recommended if the substance is to be further treated in the watch-glasses or crucible, if it is not of a ature to adhere, or if adherent particles may be rinsed away with water. If the substance is to be treated in a flask or beaker with a concentrated solvent, it is better to weigh off in a small glass tube sealed at one end. In this case the operator should know the approximate weight of the tube. When the tube has been filled with the substance, it is weighed exactly, nearly the whole quantity or a suitable portion is then shaken out into the flask or beaker, the tube is weighed again and the loss of weight shows the amount of substance taken. For hygroscopic substances the tube should be closed; the arrangement represented in fig. 43 will generally answer the purpose.

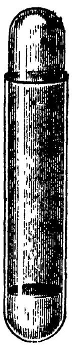

Fig. 43.

If *several* quantities of a substance are to be operated upon, the best way is to weigh off the several portions successively; which may be accomplished most readily by weighing in a glass tube the whole amount of substance, and then shaking out of the tube the quantities required one after another into appropriate vessels, weighing the tube after each time. The work may often also be materially lightened, by weighing off a large portion of the substance, dissolving this to $\frac{1}{4}$, $\frac{1}{2}$ or 1 litre, and taking out for the several estimations aliquot parts, with the 50 or 100 c.c. pipette. The first and most essential condition of this proceeding, of course, is that the pipettes must accurately correspond with the measuring flasks (§§ 18 and 20).

§ 34.

2. Estimation of Water.

If the substance to be examined—after having been freed from moisture by a suitable drying process (§§ 26 to 32)—contains water, it is usual to begin by determining the amount of this water. This operation is generally simple; in some instances, however, it has its difficulties. This depends upon various circumstances—viz., whether the compounds yield their water readily or not; whether they can bear a red heat without suffering decomposition; or whether, on the contrary, they give off other volatile substances, besides water, even at a lower temperature.

The correct knowledge of the constitution of a compound depends frequently upon the accurate estimation of the water contained in it; in many cases—for instance, in the analysis of the salts of known acids—the estimation of the water alone is sufficient to fix the formula. The estimation of water is, therefore, one of the most important, as well as most frequently occurring operations of quantitative analysis. It may be effected in two ways—viz., *a*, from the loss of weight consequent upon the expulsion of the water; *b*, by weighing the amount of water expelled.

§ 35.

a. ESTIMATION OF WATER FROM THE LOSS OF WEIGHT.

This method, on account of its simplicity, is most frequently employed. The mode of proceeding depends upon the nature of the substance.

a. The substance bears ignition without losing other constituents besides water, and without absorbing oxygen.—The substance is weighed in a platinum or porcelain crucible, and placed over the gas- or spirit-lamp; the heat should be very gentle at first, and gradually increased. When the crucible has been maintained some time at a red heat, it is allowed to cool a little, put still warm under the desiccator, and finally weighed when cold. The ignition is then repeated, and the weight again ascertained. If no further diminution of weight has taken place, the process is at an end, the desired object being fully attained. But if the weight is less than after the first heating, the operation must be repeated until the weight remains constant.

In the case of silicates, the heat must be raised to a very high degree, since many of them (*e.g.* talc, steatite, nephrite), only begin at a red heat to give off water, and require a yellow heat for the complete expulsion of that constituent (TH. SCHEERER).* Such bodies are therefore ignited over the bellows blowpipe. If any coloration of the flame is observed, this indicates volatilization of alkalies.

In the case of substances that have a tendency to intumesce, or spirt, a small flask or retort may sometimes be advantageously substituted for the crucible. Care must be taken to remove the last traces of aqueous vapor from the vessel, by suction through a glass tube.

Decrepitating salts (chloride of sodium, for instance) are put—finely pulverized, if possible—in a small covered platinum crucible, which is then placed in a large one, also covered; the whole is weighed, then heated, gently at first for some time, then more strongly; finally, after cooling, weighed again.

β. The substance loses on ignition other constituents besides water, (boracic acid, sulphuric acid, fluoride of silicon, &c.)—Here the analyst has to consider, in the first place, whether the water may not be expelled at a lower degree of heat, which does not involve the loss of other constituents. If this may be done, the substance is heated either in the water-bath, or where a higher temperature is required, in the air- or oil-bath, the temperature being regulated by the thermometer. The expulsion of the water may be promoted by a current of air (compare §§ 29 and 30); or by the addition of pure dry sand to the substance, to keep it porous.[*] The process must be continued under these circumstances also, until the weight remains constant.

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* Jahresber. von LIEBIG u. KOPP, 1851, 610.

In cases where, for some reason or other, such gentle heating is insufficient, the analyst has to consider whether the desired end may not be attained at a red heat, by adding some substance that will retain the volatile constituent whose loss is apprehended. Thus, for instance, the crystallized sulphate of alumina loses at a red heat, besides water, also sulphuric acid; now, the loss of the latter constituent may be guarded against, by adding to the sulphate an excess (about six times the quantity) of finely pulverized, recently ignited, pure oxide of lead. But the addition of this substance will not prevent the escape of fluoride of silicon from silicates when exposed to a red heat (List[†]). Thus again, the amount of water in commercial iodine may be determined by triturating it with eight times the quantity of mercury, and drying the mixture at 100° (Bolley[‡]). For the estimation of water in compounds containing silicon and fluorine, magnesia is added to the substance. For this purpose calcined magnesia in amount about twice that of the substance is ignited in a platinum crucible, then weighed, and stirred with warm water to a thick paste, the weighed substance is added and mixed up with a platinum wire of known weight, more water is added if necessary, and lastly, the mixture is cautiously dried and ignited. The loss of weight is equal to the water contained in the substance, for the products of the decomposition, fluoride of magnesium, silicic acid, and metallic oxide, weigh the same as the anhydrous substance and the magnesia. If the separated metallic oxide takes up oxygen by ignition in the air (such as protoxide of iron) a correction will of course be necessary (F. Stolba[§]).

γ. *The substance contains several differently combined quantities of water, which require different degrees of temperature for expulsion.*—Substances of this nature are heated first in the water-bath, until their weight remains constant; they are then exposed in the oil- or air-bath to 150, 200, or 250°, &c., and finally, when practicable, ignited over a gas- or spirit-lamp. In such experiments I prefer the apparatus, fig. 38. The bulb-tube may be replaced by a tube of uniform width, in which slides a little porcelain boat for the reception of the substance. In order to prevent the dehydrated substance attracting water while on the balance the boat is always weighed in a corked glass tube. In this manner differently combined quantities of water may be distinguished, and correctly estimated. Thus, for instance, crystallized sulphate of copper contains 28·87 per cent. of water, which escapes at a temperature below 140°, and 7·22 per cent., which escapes only at a temperature between 220° and 260°. It is often advisable to assist the action of heat by rarefaction of the air. Thus sulphate of magnesia, when dried *in vacuo*, over sulphuric acid at 100°, loses 5 eq. water; dried in the air at 132°, it loses the sixth, and at a moderate red heat, the seventh equivalent of water.

δ. *When the substance has a tendency to absorb oxygen* (from the presence of protoxide of iron, for instance) the water is better determined in the direct way, than by the loss (§ 36).

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[*] Ann. d. Chem. u. Pharm. 53, 233.

[†] *Ib.* 81, 189.

[‡] Dingler's Polyt. Journ. 126, 39.

[§] Zeitschr. f. anal. Chem. 7, 93.

§ 36.

b. Estimation of Water by Direct Weighing.

This method is resorted to by way of control, or in the case of substances which, upon ignition, lose, besides water, other constituents, which cannot be retained even by the addition of some other substance (*e.g.*, carbonic acid, oxygen), or in the case of substances containing bodies inclined to oxidation (*e.g.*, protoxide of iron). The principle of the method is to expel the water by the application of a red heat, so as to admit of the condensation of the aqueous vapor, and the collection of the condensed water in an appropriate apparatus, partly physically, partly by the agency of some hygroscopic substance. The increase in the weight of this apparatus represents the quantity of the water expelled.

The operation may be conducted in various ways; the following, however, is one of the most appropriate:—

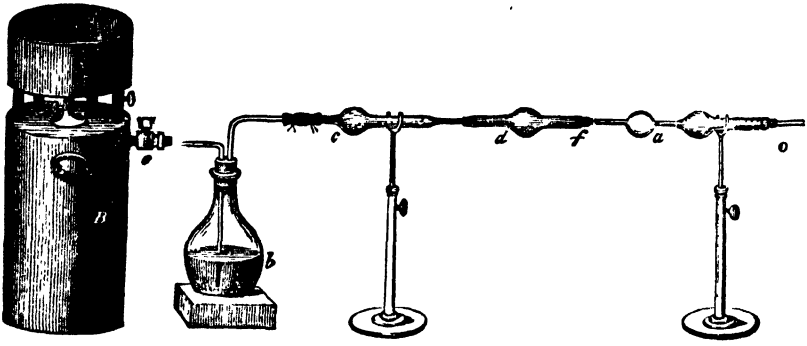

Fig. 44.

B represents a gasometer filled with air; *b* a flask half filled with concentrated sulphuric acid; *c* and *a o* are chloride of calcium tubes; *d* is a bulb-tube. The substance is weighed in the perfectly dry tube *d*, which is then connected with *c* and the weighed chloride of calcium tube *a o*, by means of sound and well-dried perforated corks. The operation is commenced by opening the stop-cock *e* a little, to allow the air, which loses all its moisture in *b* and *c*, to pass slowly through *d*; the tube *d* is then heated to beyond the boiling-point of water, by holding a lamp towards *f*, taking care not to burn the cork; and finally, the bulb which contains the substance is exposed to a low red heat, the temperature at *f* being maintained all the while at the point indicated. When the expulsion of the water has been accomplished, a slow current of air is still kept up till the bulb-tube is cold; the apparatus is then disconnected, and the chloride of calcium tube *a o*, weighed. The increase in the weight of this tube represents the quantity of water present in the substance. The empty bulb *a*, in which the greater portion of the water collects, is intended not only to prevent the liquefaction of the chloride of calcium, but enables the analyst also to test the condensed water as to its reaction and purity.

The apparatus may, of course, be modified in various ways; thus, the chloride of calcium tubes may be U-shaped; a U-tube, filled with pieces of pumice-stone saturated with sulphuric acid, may be substituted for the flask with sulphuric acid; and the gasometer may be replaced by an aspirator (fig. 34) joined to *o*. The tube *c* may not be omitted, for I have found* that air after being dried by sulphuric acid, takes up moisture from chloride of calcium. If *c* were omitted, the air escaping at *o* would be slightly moister than the air entering the bulb-tube, and consequently a little water would be lost.

The expulsion of the aqueous vapor from the tube containing the substance, may be effected also by other means than a current of air supplied by a gasometer, aspirator, or hydraulic air-pump; viz., the substance may be ignited in a dry tube, with carbonate of lead, since the carbonic acid of the latter, escaping at a red heat, serves here the same purpose as a stream of air. This method is principally applied in cases where it is desirable to retain an acid which otherwise would volatilize with the water; thus, it is applied, for instance, for the direct estimation of the water in bisulphate of potassa, &c.

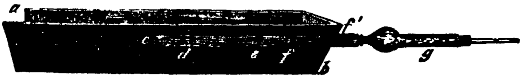

Fig. 45.

Fig. 45 represents the disposition of the apparatus.

ab is a common combustion furnace; *cf′* a tube filled as follows;—from *c* to *d* with carbonate of lead,† from *d* to *e* the substance intimately mixed with carbonate of lead, and from *e* to *f* pure carbonate of lead. The chloride of calcium tube *g*, being accurately weighed, is connected by means of a well-dried perforated cork, *f′*. The operation is commenced by surrounding the tube with red-hot charcoal, advancing from *f′* towards *c*; the fore part of the tube which protrudes from the furnace should be maintained at a degree of heat which barely permits the operator to lay hold of it with his fingers. All further particulars of this operation will be found under Organic Analysis. The mixing is performed best in the tube with a wire. The tube *cf′* may be short and moderately narrow. The charcoal furnace may, of course, be replaced by a gas furnace.

The volatilization of an acid cannot in all cases be prevented by oxide of lead; thus, for instance, we could not determine the water in crystallized boracic acid by the above process. This could readily be done, however, by igniting the acid mixed with excess of dry carbonate of soda in a glass tube drawn out behind like an erect tail, receiving the water in a chloride of calcium tube, and sweeping the residual vapor into the chloride of calcium tube by suction, after the point of the tail has been broken off. (See Organic Analysis.)

The foregoing methods for the direct estimation of water do not, however, embrace all cases in which the methods described in § 35 are inapplicable; since they can be employed, only if the substances escaping with the water are such as will not wholly or partly condense in the chloride of calcium tube (or in a tube filled with potash or with pumice-stone saturated with sulphuric acid, which might be used instead). Thus they are perfectly well adapted for determining the water in the basic carbonate of zinc, but they cannot be applied to determine the water in sulphate of soda and ammonia. With substances like the latter, we must either have recourse to the processes of organic analysis, or we must rest satisfied with the indirect estimation of the water.

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* Zeitschr. f. anal. Chem. 4, 177.

† The carbonate of lead must have been previously ignited to incipient decomposition, and cooled in a closed tube.

§ 37.

3. Solution of Substances.

Before pursuing the analytical process further, it is in most cases necessary to obtain a solution of the substance. This operation is simple where the body may be dissolved by direct treatment with water, or acids, or alkalies, &c.; but it is more complicated in cases where the body requires fusion as an indispensable preliminary to solution.

When we have mixed substances to operate upon, the component parts of which behave differently with solvents, it is not by any means necessary to dissolve the whole substance at first; on the contrary, the separation may, in such cases, be often effected, in the most simple and expeditious manner, by the solvents themselves. Thus, for instance, a mixture of nitrate of potassa, carbonate of zinc, and sulphate of baryta, may be readily and accurately analysed by dissolving out, in the first place, the nitrate of potassa with water, and subsequently the carbonate of zinc by hydrochloric acid, leaving the insoluble sulphate of baryta.

§ 38.

a. Direct Solution.

The direct solution of substances is effected, according to circumstances, in beakers, flasks or dishes, and may, if necessary, be promoted by the application of heat; for which purpose the water-bath will be found most convenient. In cases where an open fire, sand-bath, iron-plate or gauze-plate is resorted to, the analyst must take care to guard against actual ebullition of the fluid, since this would render a loss of substance from spirting almost unavoidable, especially when the process is conducted in a dish. Fluids containing a sediment, either insoluble, or, at least, not yet dissolved, will, when heated over the lamp, often bump and spirt even at temperatures far short of the boiling-point.

In cases where the solution of a substance is attended with evolution of gas, the process is conducted in a flask, placed in a sloping position, so that the spirting drops may be thrown against the walls of the vessel, and thus secured from being carried off with the stream of the evolved gas; or it may be conducted in a beaker, covered with a large watch-glass, which, after the solution is effected, and the gas expelled by gentle heating, must be thoroughly rinsed with the washing bottle.

In cases where the solution has to be effected by means of concentrated volatile acids (hydrochloric acid, nitric acid, aqua regia), the operation should never be conducted in a dish, but always in a flask covered with a watch-glass, or placed in a slanting position, and the application of too high a temperature must be avoided. The operation should always be conducted also under a hood, with proper draught, to carry off the escaping acid vapors. No arrangements for carrying off fumes can be recommended in which the flasks are closed by corks or india-rubber stoppers, as the latter are attacked by acids and the solutions may be contaminated by organic substances, sulphuric acid (from the sulphur of the india-rubber) and other matters. It is often necessary, in conducting a process of solution, to guard against the action of the atmospheric oxygen ; in such cases, a slow stream of carbonic acid is transmitted through the flask ; in some cases it is sufficient to expel the air, by simply putting a little bicarbonate of soda into the flask, containing an excess of acid, before introducing the substance.

In selecting vessels for use in this operation, it must be remembered that their substance is liable to be attacked by the solvent. As a general rule we may say that glass is slightly acted on by acids, and strongly by alkalies. Comp. § 41.

§ 39.

b. Solution, preceded by Fusion.

Substances insoluble in water, acids, or aqueous alkalies, usually require decomposition by fusion, to prepare them for analysis. Substances of this kind are often met with in the mineral kingdom ; most silicates, the sulphates of the alkaline earths, chrome ironstone, &c., belong to this class.

The object and general features of the process of fusion have already been treated of in the Qualitative Analysis. The special methods of conducting this important operation will be described under The Analysis of Silicates, and in the proper places ; as a satisfactory description of the process, with its various modifications, cannot well be given without entering more minutely into the particular circumstances of the several special cases.

Decomposition by fusion often requires a higher temperature than is attainable with a spirit-lamp with double draught, or with a common gas-lamp. In such cases, the glass-blower's lamp, fed with gas, is used with advantage.

§ 40.

4. Conversion of the dissolved Substance into a weighable Form.

The conversion of a substance in a state of solution into a form adapted for weighing may be effected either by *evaporation* or by *precipitation*.

The former of these operations is applicable only in cases where the substance, the weight of which we are desirous to ascertain, either exists already in the form suitable for the determination of its weight, or may be converted into such form by evaporation in conjunction with some reagent. The solution must, moreover, contain the substance unmixed, or, at least, mixed only with such bodies as are expelled by evaporation or ignition. Thus, for instance, the amount of sulphate of soda present in an aqueous solution of that substance may be ascertained by simple evaporation ; whilst the carbonate of potassa contained in a solution had always better be converted into chloride of potassium, by evaporating with solution of chloride of ammonium.

Precipitation may always be resorted to, whenever the substance in solution admits of being converted into a combination which is insoluble in the menstruum present, provided that the precipitate is fit for determination, which can never be the case unless it can be washed and is of constant composition after drying or ignition.

§ 41.

a. EVAPORATION.

In processes of evaporation for pharmaceutical or technico-chemical purposes the principal object to be considered is saving of time and fuel; but in evaporating processes in quantitative analysis this is merely a subordinate point, and the analyst has to direct his principal care and attention to the means of guarding against loss or contamination of the substance operated upon.

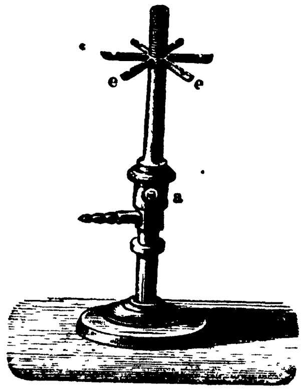

Fig. 46.

The simplest case of evaporation is when we have to *concentrate the clear fluid, without carrying the process to dryness.* To effect this object, the fluid is poured into a basin, which should not be filled more than two-thirds. Heat is then applied by placing the basin either on a water-bath, sand-bath, common stove, or heated iron plate, or over the flame of a gas- or spirit-lamp, care being taken always to guard against actual ebullition, as this invariably and unavoidably leads to loss from small drops of fluid spirting out. Evaporation over a gas- or spirit-lamp, when conducted with proper care, is an expeditious and cleanly process. BUNSEN'S gas-lamp (fig. 46), which has already been described in the Qualitative Analysis, may be used most advantageously in operations of this kind; a little wire-gauze cap, loosely fitted upon the tube of the lamp, is a material improvement. By means of this simple arrangement it is easy to produce even the smallest flame, without the least apprehension of ignition of the gas within the tube.

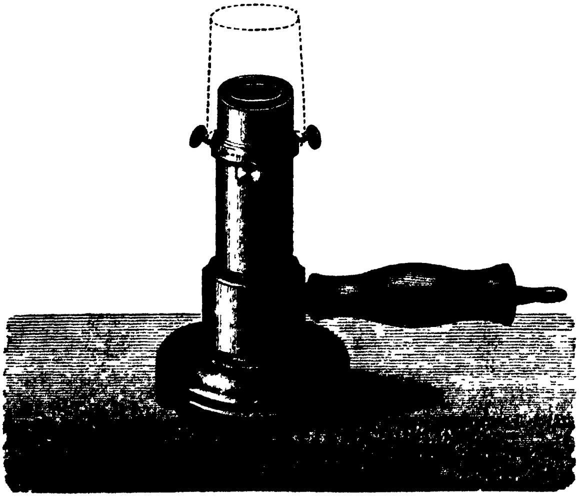

Fig. 47.

The lamp (fig. 47) lately introduced by the Brothers **Maste**, I can very highly recommend both for evaporation and ignition. It has a burner like that of **Berzelius**'s spirit-lamp, and gives a small or a very powerful flame equally well. I have had these lamps in use in my laboratory for a long time, and am much pleased with them. They are made of five different sizes.

For evaporating in dishes the furnace shown in fig. 48 is also admirably adapted. The heat in this case may be so reduced that the contents of the dish will evaporate quickly without boiling.

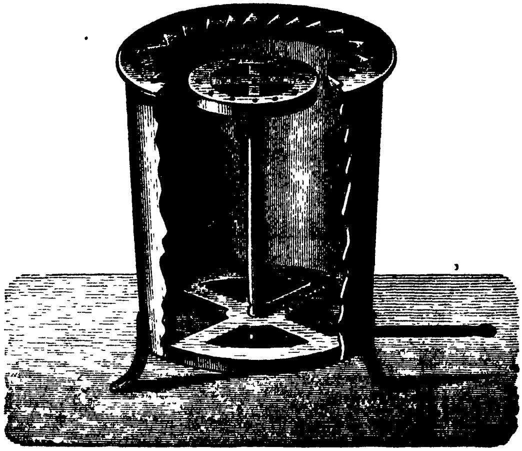
Fig. 48.

If the evaporation is to be effected on the water-bath, and the operator happens to possess a **Beindorf**, or other similarly-constructed steam apparatus, the evaporating-dish may be placed simply on an opening corresponding in size. Otherwise recourse must be had to the water-bath, fig. 49. It is made of strong sheet copper, and when used is half filled with water, which is kept boiling over a gas- or spirit-lamp. The breadth from *a* to *b* should be from 12 to 18 cm. Various flat rings of the same outside diameter as the top of the bath, and adapted to receive dishes and crucibles of different sizes, are essential adjuncts to the bath. These rings when required are simply laid on the bath.

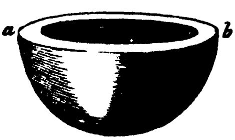

Fig. 49.

It will occasionally happen that the water in the bath completely evaporates without the operator being aware of it; this is a great inconvenience, as it will often occur, in such cases, that residues are heated to a higher degree than desirable; that concentrated solutions spirt, &c. I therefore employ in my own laboratory, a water-bath with constant level (see fig. 50). The apparatus consists of a zinc vessel, *a b c d*, 10 cm. high, 12 cm. in diameter; this is connected with the water-bath, *g*, by means of india-rubber, *e*, and a copper tube, *f*. A bottle, *h i k l*, made of sheet zinc, and filled with water, is inverted into the vessel *a b c d*; the cylindrical part of the bottle is 17 cm. high, the diameter of the neck 3 cm.; the true orifice of the bottle, which is 15 mm. wide, is at the beginning of the neck; in the inverted position this orifice is closed by the valve, *m*. Upon inverting the bottle into *a b c d*, the wire *n*, striking upon the bottom of the vessel, opens the valve. By raising or lowering the pillar-support *o*, it is easy to establish any desired level in *g*, which will remain unaltered so long as there is any water left in the bottle. The tube *f* is bent downward in the water-bath nearly to the bottom.

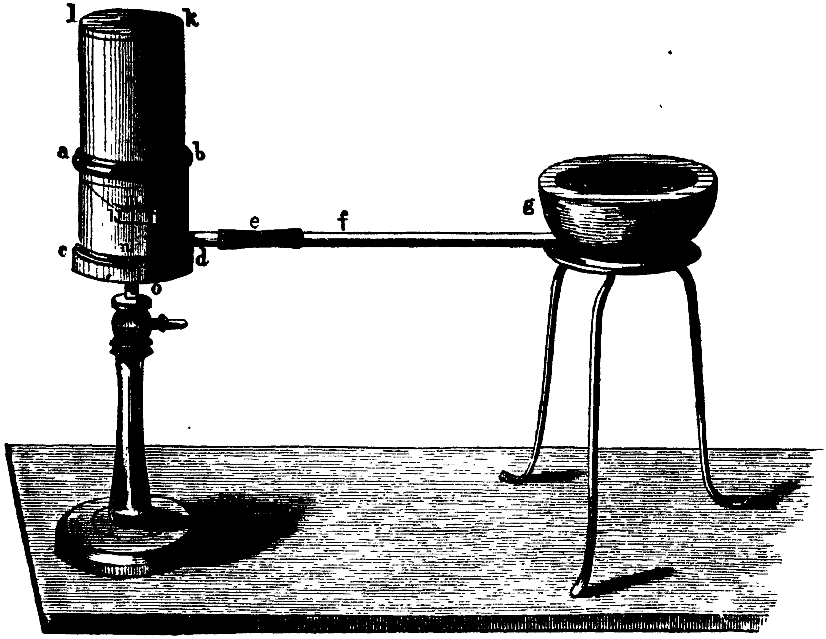

Fig. 50.

A simple arrangement for extinguishing the flame when the water is dried up is described by K. Reuss,* and Bunsen's construction for constant water-baths is described by W. H. Wahl.†

If the operator can conduct his processes of evaporation in a room set apart for the purpose, where he may easily guard against any occurrence tending to suspend dust in the air, he will find it no very difficult task to keep the evaporating fluid clean; in this case it is best to leave the dishes uncovered.‡ But in a large laboratory, where several are working, or in a room exposed to draughts of air, or in which coal fires are burning, the greatest caution is required to protect the evaporating fluid from contamination by dust or ashes. For this purpose the evaporating dish is either covered with a sheet of filtering paper, or a glass rod twisted into a triangular shape (fig. 51) is laid upon it, and a sheet of filtering-paper placed over it, which is kept in position by a glass rod laid across, the latter again being kept from rolling down by the slightly turned up ends, *a* and *b*, of the triangle. The best way, however, is the following:—Take two thin wooden hoops (fig. 52), one of which fits loosely in the other; place a sheet of blotting-paper on the smaller one, and push the other over it. This forms a cover admirably adapted to the purpose; and whilst in no way interfering with the operation, it completely protects the fluid from dust, and may be readily taken off; the paper cannot dip into the fluid; the cover lasts a long time, and may, moreover, at any time be easily renewed.

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* Zeitschr. f. anal. Chem. 9, 336. † *Ibid.* 10, 88.

‡ In my own laboratory, evaporating processes in quantitative researches are conducted in separate closets. The floor and roof of these closets should be constructed of slabs of sandstone, and the walls of brick, lined with glazed tiles or plaster of Paris. At the topmost part of the back wall is a horizontal channel of sufficient width, which at a short distance opens into a separate Russian chimney. No fire must ever be made under this chimney; but it is most desirable to have it placed quite close to another chimney, which is kept constantly warm by a fire (that of the steam apparatus, for instance). The front wall of the evaporating closet is formed of sandstone pillars eighteen decimetres high, in which are fitted sliding windows with wooden frames.

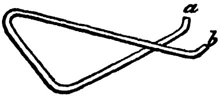

Fig. 51.

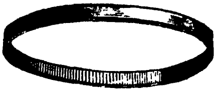
Fig. 52.

It must be borne in mind, however, that the common filtering-paper contains always certain substances soluble in acids, such as lime, sesquioxide of iron, &c., which, were covers of the kind just described used over evaporating dishes containing a fluid evolving acid vapors, would infallibly dissolve in these vapors, and the solution dripping down into the evaporating fluid, would speedily contaminate it. Care must be taken, therefore, in such cases, to use only such filtering paper as has been freed by washing from substances soluble in acids.

Evaporation for the purpose of concentration may be effected also in flasks; these are only half filled, and placed in a slanting position. The process may be conducted on the sand-bath, or over a gas- or spirit-lamp, or even, and with equal propriety, over a fire. Where the operation is conducted over a lamp or a charcoal fire, it is the safest way to place the flasks on wire gauze. Gentle ebullition of the fluid can do no harm here, since the slanting position of the flask guards effectively against risk of loss from the spirting of the liquid. Still better than in flasks the object may be attained by evaporating in tubulated retorts with open tubulure and neck directed obliquely upwards. The latter acts as a chimney, and the constant change air thus effected is extremely favorable to evaporation.

The evaporation of fluids containing a precipitate is best conducted on the water-bath; since on the sand-bath, or over the lamp, it is next to impossible to guard against loss from bumping. This bumping is occasioned by slight explosions of steam, arising from the sediment impeding the uniform diffusion of the heat. Still there remains another, though less safe way, viz., to conduct the evaporation in a crucible placed in a slanting position, as illustrated in fig. 53. In this process, the flame is made to play upon the crucible above the level of the fluid.

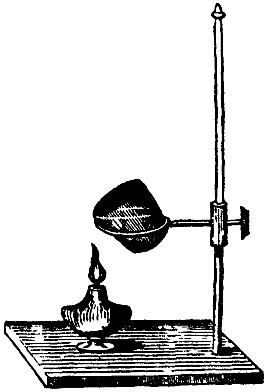
Fig. 53.

Where a fluid has to be evaporated to dryness, as is so often the case, the operation should always, if possible, be terminated on the water-bath. Where the nature of the dissolved substance precludes the application of the water-bath, the object in view may often be most readily attained by heating the contents of the dish from the top, which is effected by placing the dish in a proper position in a drying closet, whose upper plate is heated by a flame (that of the water- or sand-bath) passing over it. If the substance is in a covered platinum dish or crucible, place the gas-lamp in such a position that the flame may act on the cover from above.

In cases where the heat has to be applied from the bottom, a method must be chosen which admits of an equal diffusion and ready regulation of the heat. An air-bath is well adapted for this purpose, *i.e.*, a dish of sheet iron, in which the porcelain or platinum dish is to be placed on a wire triangle, so that the two vessels may be at all points ¼ to ½ inch distant from each other. The copper apparatus, fig. 49, may also serve as an air-bath, although I must not omit to mention that this mode of application will in the end seriously injure it. If the operation has to be conducted over a lamp, the dish should be placed high above the flame; best on wire gauze, since this will greatly contribute to an equal diffusion of the heat. The use of the sand-bath is objectionable here, because with that apparatus we cannot reduce the heat so speedily as may be desirable. An iron plate, or gauze plate, heated by gas may perhaps be used with advantage. But no matter which method be employed, this rule applies equally to all of them; that the operator must watch the process, from the moment that the residue begins to thicken, in order to prevent spirting, by reducing the heat, and breaking the pellicles which form on the surface, with a glass rod, or a platinum wire or spatula.

Saline solutions that have a tendency, upon evaporation, to creep up the sides of the vessel, and may thus finally pass over the brim of the latter, thereby involving the risk of a loss of substance, should be heated from the top, in the way just indicated; since by that means the sides of the vessel will get heated sufficiently to cause the instantaneous evaporation of the ascending liquid, preventing thus its overflowing the brim. The inconvenience just alluded to may, however, be obviated also, in most cases, by covering the brim, and the uppermost part of the inner side of the vessel, with a very thin coat of tallow, thus diminishing the adhesion between the fluid and the vessel.

In the case of liquids evolving gas bubbles upon evaporating, particular caution is required to guard against loss from spirting. The safest way is to heat such liquids in an obliquely-placed flask, or in a beaker covered with a large watch-glass; the latter is removed as soon as the evolution of gas bubbles has ceased, and carefully rinsed into the glass, by means of a washing-bottle. If the evaporation has to be conducted in a dish, a rather capacious one should be selected, and a very moderate degree of heat applied at first, and until the evolution of gas has nearly ceased.

If a fluid has to be evaporated *with exclusion of air*, the best way is to place the dish under the bell of an air-pump, over a vessel with sulphuric acid, and to exhaust; or a tubulated retort may be used, through whose tubulure hydrogen or carbonic acid is passed by the aid of a tube not quite reaching to the surface of the fluid.

The material of the evaporating vessels may exercise a much greater influence on the results of an analysis than is generally believed. Many rather startling phenomena that are observed in analytical processes may arise simply from contamination by the material of the vessel; great errors may also spring from the same source.*

The importance of this point induced me some time ago to subject it to a careful investigation (see Appendix, Experiments, 1—4) and more recently A. **Emmerling**† has still more thoroughly examined the matter, and arrived at results which substantially agree with mine.

Distilled water kept boiling for some length of time in glass (flasks of Bohemian glass) dissolves very appreciable traces of that material. This is owing to the formation of soluble silicates; the particles dissolved consist chiefly of potassa, or soda and lime, in combination with silicic acid. A much larger proportion of the glass is dissolved by water containing caustic or carbonated alkali; boiling solution of chloride of ammonium also strongly attacks glass vessels. This is especially the case with new flasks; flasks in which chloride of ammonium had been boiled for some time lost far less on boiling with fresh chloride of ammonium than on boiling with water. Boiling dilute acids, with the exception, of course, of hydrofluoric and hydrofluosilicic acids, exercise a less powerful solvent action than pure water. Porcelain (Berlin dishes) is much less affected by water than glass; alkaline liquids also exercise a much less powerful solvent action on porcelain than on glass; the quantity dissolved is, however, still notable. Solution of chloride of ammonium acts on porcelain as strongly as on glass; dilute acids, though exercising no very powerful action on porcelain, yet attack that material more strongly than glass. It results from these data, that in analyses pretending to a high degree of accuracy, platinum or silver dishes should always be preferred. The former may be used in all cases where no free chlorine, bromine, or iodine is present in the fluid, or can be formed during evaporation. Fluids containing caustic alkalies may safely be evaporated in platinum, but not to the point of fusion of the residue. Silver vessels should never be used to evaporate acid fluids or liquids containing alkaline sulphides; but they are admirably suited for solutions of caustic and carbonated alkalies. Where the use of porcelain or glass cannot be avoided, as in the evaporation of large amounts of fluid, porcelain generally deserves the preference; glass vessels should never be used in accurate analyses for alkaline fluids.

§ 42.

We come now to *weighing the residues remaining upon the evaporation of fluids.* We allude here simply to such as are soluble in water; those which are separated by filtration will be treated of afterwards. Residues are generally weighed in the same vessel in which the evaporation has been completed, for which purpose platinum dishes, from 4 to 8 cm. in diameter, provided with light covers, or large platinum crucibles, are best adapted, since they are lighter than porcelain vessels of the same capacity.

However, in most cases, the amount of liquid to be evaporated is too large for so small a vessel, and its evaporation in portions would occupy too much time. The best way, in cases of this kind, is to concentrate the liquid first in a larger vessel, and to terminate the operation afterwards in the smaller weighing vessel. In transferring the fluid from the larger to the smaller vessel, the lip of the former is slightly greased, and the liquid made to run down a glass rod (fig. 54). Finally the large vessel is carefully rinsed with a washing-bottle, until a drop of the last rinsing leaves no residue upon evaporation on a platinum knife. When the fluid has thus been transferred to the weighing vessel, the evaporation is completed on the water-bath, and the residuary substance either ignited or dried. *If it is to be ignited* the dish is covered with a lid of thin platinum (or a thin glass plate), and then placed high over the flame of a lamp, and heated very gently until all the water which may still adhere to the substance is expelled; the dish is now exposed to a stronger, and finally to a red-heat. (Where a glass plate is used, this must, of course, be removed before igniting.) It is well to make the flame play obliquely on the cover from above, so as to run as little risk as possible of loss by spirting. After cooling in a desiccator, the covered dish is weighed with its contents. When operating upon substances which decrepitate, such as chloride of sodium, for instance, it is advisable to expose them—after their removal from the water-bath, and previously to the application of a naked flame—to a temperature somewhat above 100°, either in the air-bath, or on a sand-bath, or on a common stove.

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* Comp. A. **Souchay**, Zeitschr. f. anal. Chem. 4, 66.

† Ann. d. Chem. u. Pharm. 150, 257; also Zeitschr. f. anal. Chem. 8. 434.

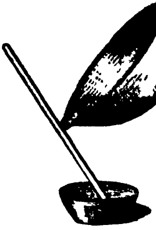

Fig. 54.

If the residue does not admit of ignition, as is the case, for instance, with organic substances, ammoniacal salts, &c., it is dried at a temperature suited to its nature. In many cases, the temperature of the water-bath is sufficiently high for this purpose, for the drying of chloride of ammonium, for instance; in others, the air- or oil-bath must be resorted to (see §§ 29 and 30). Under any circumstances, the drying must be continued until the substance ceases to suffer the slightest diminution in weight, after renewed exposure to heat for half an hour. The dish should invariably be covered during the process of weighing.

As saline residues left on evaporation when ignited or dried often have a tendency to attract moisture, the first weighing, which always takes some length of time, frequently gives too high a result. It is well therefore, after this, to heat again, allow to cool in the desiccator, then place the first found weights on the balance, and afterwards the dish; in which way the time spent in the actual weighing will be reduced to a minimum and the dish will not be needlessly exposed to the atmosphere.

If, as will frequently happen, we have to deal with a fluid containing a small quantity of a salt of potassa or soda, the weight of which we want to ascertain, in presence of a comparatively large amount of a salt of ammonia, which has been mixed with it in the course of the analytical process, I prefer the following method. The saline mass is thoroughly dried, in a large dish, on the water-bath, or, towards the end of the process, at a temperature somewhat exceeding 100°. The dry mass is then, with the aid of a platinum spatula, transferred to a small glass dish, which is put aside for a time in a desiccator. The last traces of the salt left adhering to the large dish are rinsed off with a little water into the small dish, or the large crucible, in which it is intended to weigh the salt; the water is then evaporated, and the dry contents of the glass dish are added to the residue; the ammonia salts are now expelled by ignition, and the residuary fixed salts finally weighed. Should some traces of the saline mass adhere to the glass dish, they ought to be removed and transferred to the weighing vessel, with the aid of a little pounded chloride of ammonium, or some other salt of ammonia, as the moistening again with water would involve an almost certain loss of substance.

§ 43.

b. PRECIPITATION.

Precipitation is resorted to in quantitative analysis far more frequently than evaporation, since it serves not merely to convert substances into forms adapted for weighing, but also, and more especially, to separate them from one another. The principal intention in precipitation is to convert the substance in solution into a form in which it is insoluble in the menstruum present. The result will, therefore, *cæteris paribus*, be the more accurate, the more the precipitated body deserves the epithet insoluble, and in cases where precipitates are of the same degree of solubility, that one will suffer the least loss, which comes in contact with the smallest amount of solvent.

Hence it follows, First, that in all cases where other circumstances do not interfere, it is preferable to precipitate substances in their most insoluble form; thus, for instance, baryta had better be precipitated as sulphate than as carbonate. Secondly, that when we have to deal with precipitates that are not quite insoluble in the menstruum present, we must endeavour to remove that menstruum, as far as practicable, by evaporation; thus a dilute solution of strontia should be concentrated, before proceeding to precipitate the strontia with sulphuric acid. And, thirdly, that when we have to deal with precipitates slightly soluble in the liquid present, but insoluble in another menstruum, into which the former may be converted by the addition of some substance or other, we ought to endeavour to bring about this modification of the menstruum; thus, for instance, alcohol may be added to water, to induce complete precipitation of chloride of platinum and ammonium, chloride of lead, sulphate of lime, &c.; thus again, the basic phosphate of magnesia and ammonia may be rendered insoluble in an aqueous menstruum by the addition of ammonia.

Precipitation is generally effected in beakers. In cases, however, where we have to precipitate from fluids in a state of ebullition, or where the precipitate requires to be kept boiling for some time with the fluid, flasks or dishes are substituted for beakers, with due regard always to the material of which they are made (see § 41, at the end).

The separation of precipitates from the fluid in which they are suspended, is effected either by decantation or filtration, or by both these processes jointly.

But, before proceeding to the separation of the precipitate by any of these methods, the operator must know whether the precipitant has been added in sufficient quantity, and whether the precipitate is completely formed. To determine the latter point, an accurate knowledge of the properties of the various precipitates must be attained, which we shall endeavour to supply in the third section. To decide the former question, it is usually sufficient to add to the fluid (after the precipitate has settled) cautiously a fresh portion of the precipitant, and to note if a further turbidity ensues. This test, however, is not infallible, when the precipitate has not the property of forming immediately; as, for instance, is the case with phospho-molybdate of ammonia. When this is apprehended, pour out (or transfer with a pipette) a small quantity of the clear supernatant fluid into another vessel, add some of the precipitant, warm, if necessary; and after some time observe whether a fresh precipitate has formed. As a general rule, the precipitated liquid should be allowed to stand at rest for several hours, before proceeding to the separation of the precipitate. This rule applies more particularly to crystalline, pulverulent, and gelatinous precipitates, whilst curdy and flocculent precipitates, more particularly when the precipitation was effected at a boiling temperature, may often be filtered off immediately. However, we must observe here, that all general rules, in this respect, are of very limited application.

§ 44.

a. SEPARATION OF PRECIPITATES BY DECANTATION.

When a precipitate subsides so completely and speedily in a fluid that the latter may be poured off perfectly clear, or drawn off with a syphon, or removed by means of a pipette, and that the washing of the precipitate does not require a very long time, decantation is often resorted to for its separation and washing; this is the case, for instance, with chloride of silver, metallic mercury, &c.

Decantation will always be found a very expeditious and accurate method of separation, if the process be conducted with due care; it is necessary, however, in most cases, to promote the speedy and complete subsidence of the precipitate; and it may be laid down as a general rule, that heating the precipitate with the fluid will produce the desired effect. Nevertheless, there are instances in which the simple application of heat will not suffice; in some cases, as with chloride of silver, for instance, agitation must be resorted to; in other cases, some reagent or other is to be added—hydrochloric acid, for instance, in the precipitation of mercury. We shall have occasion, subsequently, in the fourth section, to discuss this point more fully, when we shall also mention the vessels best adapted for the application of this process to the various precipitates.

After having washed the precipitate repeatedly with fresh quantities of the proper fluid, until there is no trace of a dissolved substance to be detected in the last rinsings, it is placed in a crucible or dish, if not already in a vessel of that description; the fluid still adhering to it is poured off as far as practicable, and the precipitate is then, according to its nature, either simply dried, or ignited.

A far larger amount of water being required for washing precipitates by decantation than on filters, the former process can be expected to yield accurate results only where the precipitates are absolutely insoluble. For the same reason, decantation is not ordinarily resorted to in cases where we have to determine other constituents in the decanted fluid.

The decanted fluid must be allowed to stand at rest from twelve to twenty-four hours, to make quite sure that it contains no particles of the precipitate ; if, after the lapse of this time, no precipitate is visible, the fluid may be thrown away ; but if a precipitate has subsided, this had better be estimated by itself, and the weight added to the main amount ; the precipitate may, in such cases, be separated from the supernatant fluid by decantation, or by filtration.

β. SEPARATION OF PRECIPITATES BY FILTRATION.

This operation is resorted to whenever decantation is impracticable, and, consequently, in the great majority of cases ; provided always the precipitate is of a nature to admit of its being completely freed, by mere washing on the filter, from all foreign substances. Where this is not the case, more particularly, therefore, with gelatinous precipitates, hydrate of alumina for instance, a combination of decantation and filtration is resorted to (§ 48.) Suction is sometimes employed to hasten the process.

§ 45.

aa. ORDINARY FILTRATION.

aa. FILTERING APPARATUS.

Filtration, as a process of quantitative analysis, is almost exclusively effected by means of paper.

Plain circular filters are most generally employed ; plaited filters are only occasionally used. Much depends upon the quality of the paper. Good filtering paper must possess the three following properties ; first, it must completely retain the finest precipitates ; secondly, it must filter rapidly ; and thirdly, it must be as free as possible from inorganic bodies, but more especially from such as are soluble in acid or alkaline fluids.

It is a matter of some difficulty, however, to procure paper fully answering these conditions. The Swedish filtering paper, with the watermark J. H. MUNKTELL, is considered the best, and, consequently, fetches the highest price ; but even this answers only the first two conditions, being by no means sufficiently pure for very accurate analyses, since it leaves upon incineration about ·3 per cent. of ash,* and yields to acids perceptible traces of lime, magnesia, and sesquioxide of iron. For exact experiments it is, consequently, necessary first to extract the paper with dilute hydrochloric acid, then to wash the acid completely out with water, and finally to dry the paper. The preparation of such exhausted filters on a large scale is described in the Qualitative Analysis. To exhaust a few filters, the best way is to place them one within the other in a funnel, as in filtering ; they are then moistened with a mixture of one part of ordinary pure hydrochloric acid with two parts of water, which is allowed to act on them for about ten minutes ; after this, all traces of the acid are carefully removed by washing the filters repeatedly with warm water. The funnel being then covered with a piece of paper, turned over the edges, is put in a warm place until the filters are dry. Filter-paper containing lead, and which is consequently blackened by sulphuretted hydrogen, should be rejected.*

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* PLANTAMOUR found the ash of Swedish filtering paper to consist of 63·28 silicic acid, 12·83 lime, 6·21 magnesia, 2·94 alumina, and 13·92 sesquioxide of iron, in 100 parts.

Ready-cut filters of various sizes should always be kept on hand. Filters are either cut by circular patterns of pasteboard or tin, or, still better, by MOHR's filter-patterns (fig. 55). This little apparatus is made of tin-plate, and consists of two parts. *B* is a quadrant fitting in *A*, whose straight edges are turned up, and which is slightly smaller than *B*. The sheets of filter-paper are first cut up into squares, which are folded in quarters and placed in *A*; then *B* is placed on the top, and the free edge of the paper is cut off with scissors. Filters cut in this way are perfectly circular and of equal size. Several pairs of these patterns of various sizes (3, 4, 5, 6·5, and 8 cm. radius) should be procured. In taking a filter for a given operation, you should always choose one which, after the fluid has run through, will not be more than half filled with the precipitate.

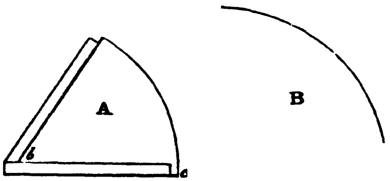

Fig. 55.

As to the funnels, it is very important that their sides should be inclined at the angle of 60°, and that they should not bulge. Glass is the most suitable material for them.

The filter should never protrude beyond the funnel. It should come up to one or two lines from the edge of the latter. The filter is firmly pressed into the funnel, to make the paper fit closely to the side of the latter; it is then moistened with water; any extra water is not poured out, but allowed to drop through.

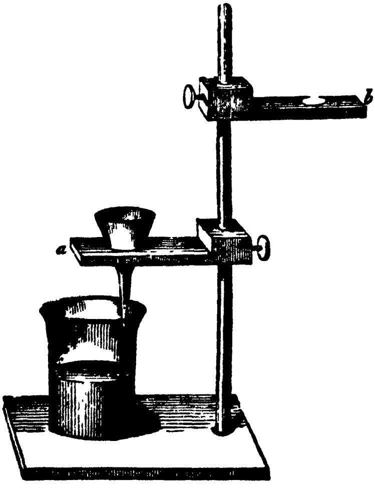

Fig. 56.

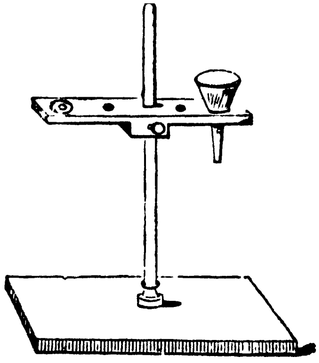

Fig. 57.

The stands shown in figs. 56 and 57 complete the apparatus for filtering. The stand in fig. 56 is more particularly adapted for the reception of larger funnels, and should therefore be made a little more solid than that in fig. 57, which is intended for the reception of funnels of smaller size. The stands are made of hard wood. The arm holding the funnel or funnels must slide easily up and down; and be fixable by the screw. The holes for the funnels must be cut conically, to keep the funnels steadily in their place. These stands are very convenient, and may be readily moved about without interfering with the operation.

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* WICKE, Annal. d. Chem. u. Pharm. 112, 127.

ββ. Rules to be observed in the Process of Filtration.

In the case of curdy, flocculent, gelatinous, or crystalline precipitates there is no danger of the fluid passing turbid through the filter. But with fine pulverulent precipitates it is generally necessary and always advisable, to let the precipitate subside, and then filter the supernatant liquid, before proceeding to place the precipitate upon the filter. We generally proceed in this way also with other kinds of precipitates, especially with those that require to stand long before they completely separate. Precipitates which have been thrown down hot, are most properly filtered off before cooling (provided always there be no objection to this course), since hot fluids run through the filter more speedily than cold ones. Some precipitates have a tendency to be carried through the filter along with the fluid; this may be prevented in some instances by modifying the latter. Thus sulphate of baryta, when filtered from an aqueous solution, passes rather easily through the filter—the addition of hydrochloric acid or chloride of ammonium prevents this in a great measure. If the operator finds, during a filtration, that the filter would be much more than half filled by the precipitate, he had better use an additional filter, and thus distribute the precipitate over the two; for, if the first were too full, the precipitate could not be properly washed.

The fluid ought never to be poured directly upon the filter, but always down a glass rod (as shown in fig. 54), and the lip or rim of the vessel from which the fluid is poured should always be slightly greased with tallow. The tallow should be poured into a porcelain crucible or a glass tube, corked at the bottom; in the latter case, as it is required for use, the cork is pushed with a glass rod. The best way of applying the tallow to the lip of a vessel is with the greased finger. If it is desired to filter the supernatant fluid without disturbing the precipitate, the rod should not be placed after use in the vessel with the precipitate, but in a separate vessel, which is to be rinsed out at the end of the operation. The stream ought invariably to be directed towards the sides of the filter, never to the centre, since this might occasion loss by splashing. The filtrate is received either in flasks, beakers, or dishes. Strict care should be taken that the drops of fluid filtering through glide down the side of the receiving vessel; they should never be allowed to fall into the centre of the filtrate, since this again might occasion loss by splashing. The best method is that shown in fig. 56, viz., to rest the point of the funnel against the upper part of the inside of the receiving vessel.

If the process of filtration is conducted in a place perfectly free from dust, there is no necessity to cover the funnel, or the vessel receiving the filtrate; however, as this is but rarely the case, it is generally indispensable to cover both. This is best effected with round plates of sheet-glass. The plate used for covering the receiving vessel should have a small U-shaped piece cut out of its edge, large enough for the tube of the funnel to go through. The effect desired may be produced by cautiously chipping out the glass bit by bit with the aid of a key. Plates perforated in the centre are worthless as regards the object in view.

After the fluid and precipitate have been transferred to the filter, and the vessel which originally contained them has been rinsed repeatedly with water, it happens generally that small particles of the precipitate remain adhering to the vessel, which cannot be removed with the glass rod. From beakers or dishes, these particles may be readily removed by means of a feather prepared for the purpose by tearing off nearly the whole of the plumules, leaving only a small piece at the end which should be cut perfectly straight. A glass rod, the end of which is tightly covered with a piece of flexible tube, may also be used. From flasks, minute portions of heavy precipitates which are not adherent, are readily removed by blowing a jet of water into the flask, held inverted over the funnel; this is effected by means of the washing-bottle shown in fig. 60, *b* being turned upwards. If the minute adhering particles of a precipitate cannot be removed by mechanical means, solution in an appropriate menstruum must be resorted to, followed by re-precipitation. Bodies for which we possess no solvent, such as sulphate of baryta, for instance, must not be precipitated in flasks.

§ 46.

γγ. Washing of Precipitates.

After having transferred the precipitate completely to the filter, we have next to perform the operation of washing; this is effected by means of one of the well-known washing bottles, figs. 58, 59, and 60.*

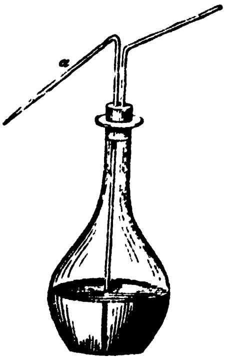

Fig. 58.

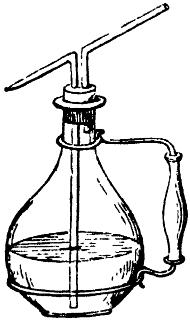

Fig. 59.

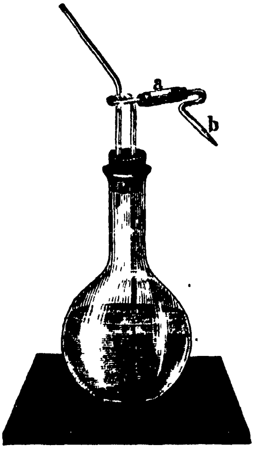

Fig. 60.

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* A washing bottle for stinking liquids has been constructed by Jacob, Zeitschr. f. anal. Chem. 5, 168.

By the arrangement shown in fig. 60, the jet may be turned in any required direction. Care must be taken that no loss is occasioned by too violent a stream of water. In cases where a precipitate has to be washed with great caution, the apparatus illustrated in fig. 61 will be found to answer very well. The construction of this apparatus does not require much explaining. The point *a* is drawn out at the end, and broken off. When the flask is inverted, it supplies a fine continuous jet of water.

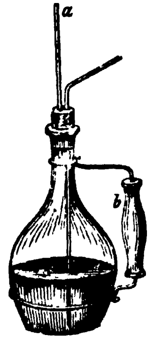

Fig. 61.

Precipitates requiring washing with water, are washed most expeditiously with hot water, provided always there be no special reason against its use. The washing-bottle shown in fig. 59 is particularly well adapted for this purpose. The wood handle which is fastened to the flask with wire serves to facilitate holding it. Instead of a handle you may have a sufficiently thick coil of string wound round the neck.

It is a rule in washing precipitates not to add fresh wash-water to the filter till the old has quite run through. In applying the jet of water you have to take care on the one hand that the upper edge of the filter is properly washed, and on the other hand that no canals are formed in the precipitate, through which the fluid runs off, without coming in contact with the whole of the precipitate. If such canals have formed and cannot be broken up by the jet, the precipitate must be stirred cautiously with a small platinum knife or glass rod.

The washing may be considered completed when all soluble matter that is to be removed has been got rid of. The beginner who devotes proper attention to the completion of this operation shuns one of the rocks which he is most likely to encounter. Whether the precipitate has been completely washed may generally be ascertained by slowly evaporating a drop of the last washings upon a platinum knife, and observing if a residue is left. But in cases where the precipitate is not altogether insoluble in water (sulphate of strontia, for instance), recourse must be had to more special tests, which we shall have occasion to point out in the course of the work. The student should never discontinue the washing of a precipitate because he simply imagines it is finished—he must be certain.

Some time ago continuous washing-bottles used to be employed for protracted washings. But they have now completely fallen into disuse in analytical laboratories, precipitates which are difficult to wash being treated as described in § 48. The objections to the use of the continuous washing-bottle* are the following: canals are liable to be formed in the precipitate, a very large quantity of water is required, and the employment of hot water is excluded.

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* Chemists interested in the construction of these apparatus are referred to the Handwörterbuch der Chemie, 2 ed., 2, 584-6.

§ 47.

bb. Filtration by Suction.

Filtration being a constantly recurring and very tedious operation, many attempts have been made to accelerate it by suction. Bunsen[*] has recently subjected the matter to an exhaustive inquiry. In order to avoid the danger of the filter breaking, which has generally prevented analysts from employing this method, it is necessary that the filter, even to the apex, should be supported by the funnel. The sides of the funnel must therefore be free from irregularities, and inclined at an angle of 60°; in it is set a little cone of very thin platinum foil exactly fitting, and then the paper is so placed that, after being moistened, it may be in contact at all points with the funnel, no air-bubbles intervening. The preparation of the little platinum cone shall be explained in Bunsen's own words:—"A funnel of the right shape is carefully selected, and in this a disc of writing-paper is fitted like a filter, so that the sides may be in perfect contact with the funnel; the upper edges of the paper are then fixed to the funnel with a few drops of sealing-wax, the paper is saturated with oil, and into this some plaster of Paris is poured, a small handle being fixed in before the plaster has set. After a few hours the plaster cone, together with the oiled paper which adheres to it, may be removed by means of the handle. The paper is again oiled on the outside, and the cone is placed in a crucible 4 or 5 cm. high, filled with plaster of Paris; when the plaster has hardened the cone is taken out, and all paper adhering to the casts is removed, if necessary, by rubbing with the finger. In this way a solid and a hollow cone are obtained, which fit exactly in each other, and correspond perfectly with the funnel. To prepare the platinum cone, a piece of foil, weighing about ·154 grm. per square cm., is cut to the shape and size represented in fig. 62, *ab* being a slit at right angles with *cd*, terminating in the centre of the circle. The foil is now softened by ignition, and the solid plaster cone is laid on it with the apex over *a*, *abd* is then pressed on the cone, and the rest of the foil is wrapped round the cone as closely as possible. Finally, the foil is again ignited and moulded to the plaster with the fingers, the hollow cone is laid on the top, and pressed tightly down. The platinum cone should, when finished, show no light through its apex, it is sufficiently firm for immediate use without any soldering."

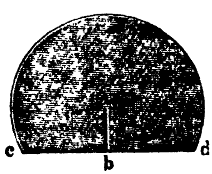

Fig. 62.

A caoutchouc stopper with two holes is chosen, into one is fitted the funnel provided with platinum cone and paper, the tube of the funnel being allowed to *project from* 5 *to* 8 *cm. from the stopper*; into the other is fitted a short tube bent at right angles, which should *not project beyond the stopper* on the inside. If the stopper is now fixed air-tight into a flask, and suction is applied to the outer end of the bent tube, the air within the flask will be rarefied; and on filling the funnel with the fluid to be filtered, the latter will be driven through the more rapidly the greater the difference between the pressure within and without the flask. If it is desired to bring about a considerable difference of pressure, an ordinary flask will not be strong enough, as it might be shattered with explosion, and consequently a flask of stout glass must be used. The flask may be conveniently placed in a stand made of tin-plate (see fig. 64), down the sides of which three strips of thick cloth or india-rubber are glued. This arrangement affords a firm stand for flasks of various sizes, and if covered with a cloth will prevent any danger from a possible explosion.

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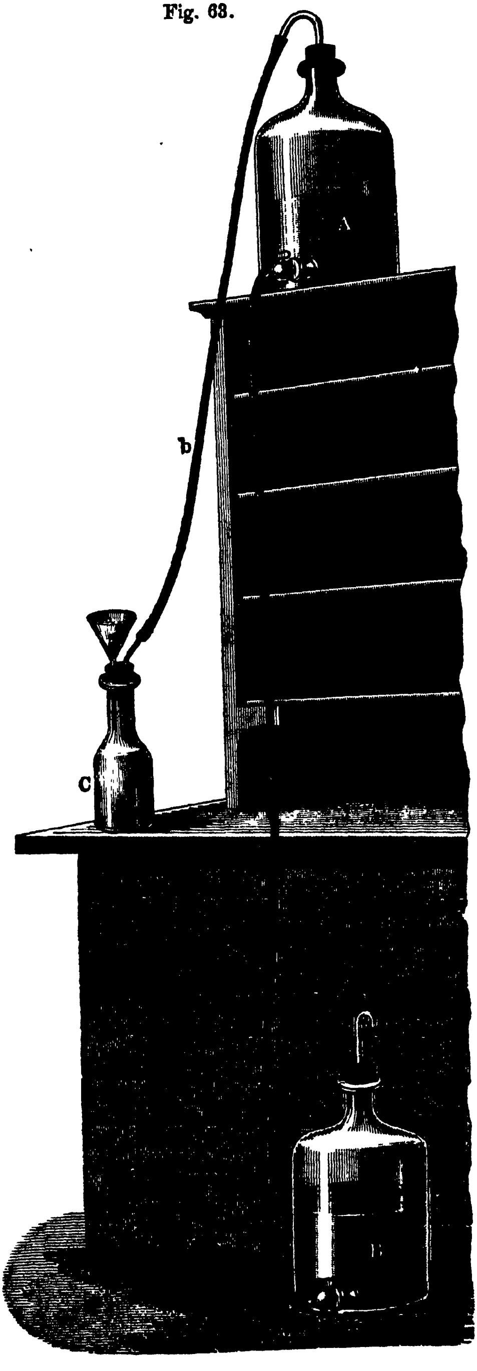
[*] Ann. d. Chem. u. Pharm. 148, 269; also Zeitschr. f. anal. Chem. 8, 174.

As an exhauster, any aspirator will serve which can reduce the pressure by a quarter of an atmosphere. A very simple arrangement is shown in fig. 63; *a* and *b* are stout india-rubber tubes, which connect *A* with *B* and *C* respectively. On opening the cocks in *A* and *B*, the water runs from the former to the latter, which causes a rarefaction in *A*, and consequently in *C*. The exhaustion is the greater the greater the distance between the water levels in the two bottles. These may be of 2 or 4 litres capacity; they should be similar, so that when the upper one is empty they may be transposed.

However, the hydraulic air-pump affords

Fig. 63.



by far the most convenient means of exhaustion, and more or less imperfect forms of this instrument had long been employed* before **Bunsen** brought it to its present high degree of perfection. Fig. 64 represents his instrument in connexion with a filtering flask, as constructed by **Desaga**, of Heidelberg. In describing it, I shall adhere almost entirely to **Bunsen**'s own words. By opening the clip *a*, the water flowing through the supply pipe *w* enters *c*, and passes away down the leaden pipe *d*, which is 8 mm. wide. This pipe leads to the bottom of a drain 30 or 40 feet below the ground.† The tube *e*, fused into *c*, reaches nearly to the bottom of *c*, and has below a small aperture. At *f* is connected a mercurial gauge. *h* is intended to retain the steam which is given off on washing with hot water. All the caoutchouc connectors consist of thick-walled tubing of 2 to 3 mm.

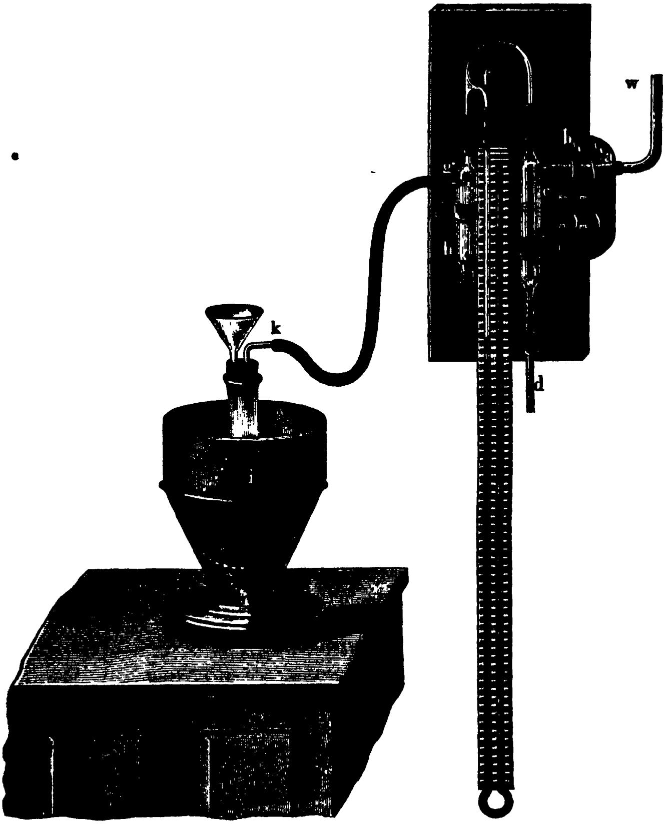


Fig. 64.

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* Compare for instance Zeitschr. f. anal. Chem. 2, 359, and 4, 46.

† If the hydraulic air-pump is in the upper part of the house, it will of course be enough to have the lead pipe reaching nearly to the bottom of a vessel in the cellar. The vessel should have a lateral aperture halfway from the bottom, connected by a lead pipe with a deep drain.

bore. The whole apparatus is secured to a board fixed to the wall. In fastening the apparatus to the board, bear in mind that the latter may warp.

When *a* is opened, the water runs down *d*, and draws air with it, which issues from the extremity of *e* in the form of a series of small bubbles. If the water runs at its fastest, even with a column 40 feet high, it is impossible from friction against the lead pipe to obtain a considerable exhaustion. We therefore have a second clip *b*, to regulate the water supply once for all, and so to reduce the friction as to obtain the maximum rarefaction when *a* is fully open. An apparatus properly regulated will, in a comparatively short time, in vessels of large size, reduce the pressure exactly to that which corresponds to the tension of aqueous vapor at the temperature of the water—namely, to from 7 to 10 mm. of mercury.

The glass at *h* should be somewhat narrowed. To effect a filtration, connect the flask *i* with the pump, then pour the supernatant clear fluid on to the filter, and afterwards the precipitate. The filtrate will first run down in a rapid stream, then in drops. The filter may be filled nearly to the edge, and this is, indeed, to be recommended. The precipitate will be compressed to a thin layer, and penetrated by channels. As soon as the fluid has ceased dropping, and the first channels are visible, the precipitate will be so firmly attached to the paper, that it will not be disturbed by water, if carefully added. The washing is completed by filling the funnel a centimetre *above* the edge of the filter, pouring the water cautiously on the side, from an open vessel—a washing bottle must not be used. After the funnel has been filled from one to four times, the washing will be finished, and if the filter is allowed to drain completely, it will often be dry enough to be transferred with the precipitate at once to the crucible and ignited, see § 52. By this method of filtering, the operation is extraordinarily shortened. The filter need not be so large as usual, as the precipitate will occupy less bulk; and precipitates, which would otherwise be very difficult to wash at all, may be completely washed with a relatively small quantity of fluid. Finally, precipitates in the dry state in which they are obtained after the filtrate has been fully sucked out, may be separated very easily and completely from the filter, even free from all fibres.

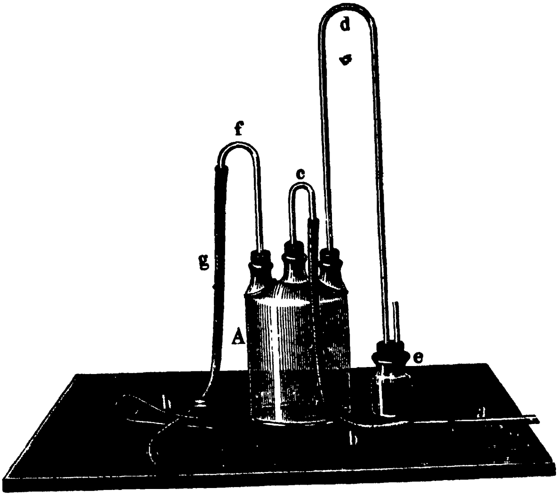

Fig. 65.

We have thus described the hydraulic air-pump in its most perfect state, as it may be used, not only for filtration, but also for all other purposes (such as the exhaustion of desiccators, &c.); but we may note that for pumps which are only to be used for filtering, and drawing air through drying apparatus (§ 28), a fall of 10 to 15 feet is sufficient. Such a fall may be obtained, even on the ground floor, and without a deep drain, by fixing the pump to the upper part of the wall. There must then, of course, be an arrangement on the ground for turning the water on and off. The tube which exhausts the air is connected in that case with a thin leaden tube, which is brought down to the bench. The device shown fig. 65 will be found convenient for this purpose. *a* is a lead pipe leading to the pump, *b* is the india-rubber tube connecting it with *c* and *A*, *d* is a glass tube of sufficient height, which dips into mercury at *e*, and serves as a gauge, the glass tube *f* is connected with the flexible tube *g*, which may be closed by means of the clip *h*. If this flexible tube is connected with the suction tube of the filtering flask, the pump is set going, and *h* is opened, the filtration will proceed.

A slight but effective suction may also be applied to filtrations without the use of air-pumps or aspirators. Arrangements with this object are shown in figs. 66 and 67. The apparatus fig. 66 is recommended by Weil.* On sucking at *c* the fluid is raised, and when the clip is closed the filtration will proceed under pressure. To strengthen the paper a small filter *a* is first inserted, and then the proper filter *b*. Both filters are fitted close to the glass, and without any rucks. Fig. 67 shows an arrangement proposed by Piccard.† If the column of water is not higher than 30 cm., the filter does not require any extra support. However, it is always advisable even in this case to insert first a small filter. If the filter lies close to the glass, and is free from rucks, the filtration will proceed much more quickly (Piccard says 10 or 12 times more quickly) than without the use of the bent tube.

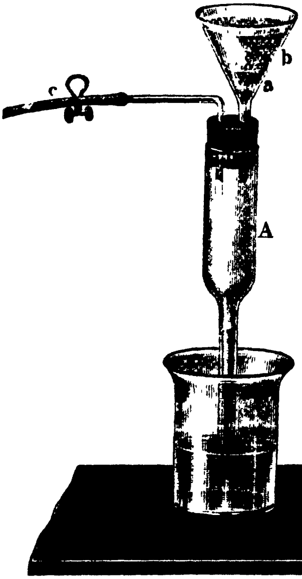

Fig. 66.

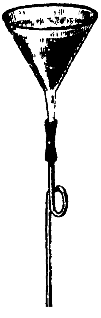

Fig. 67.

Arrangements for exhausting the air render it possible occasionally to dispense entirely with paper and to filter through asbestos or powdered glass; such filters will be found especially useful when

* Zeitschr. f. anal. Chem. 2, 359.

† *Ib.* 4, 47.

a precipitate has to be dried at a certain temperature, and then weighed.

Fig. 68 is a filter tube which I have recommended for weighing small quantities of sulphide of antimony.* After the tube has been charged at *a* with asbestos in long fibres, a little water is passed through to remove loose particles of the latter, the tube is fixed in a perpendicular position, and suction is applied at *b*, finally with appropriate heating, in order to dry the filter completely. It is then weighed, *b* is fixed into the stopper of the filtering flask, a small funnel is placed on *i*, gentle suction is applied and the fluid to be filtered is poured in cautiously.

Fig. 69 is a glass or sand filter recommended by W. GIBBS and TAYLOR† for a similar purpose. The tube contains at *a* first fragments of glass, then coarse powder, and finally fine powder.

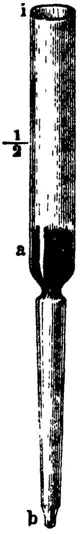

Fig. 68.

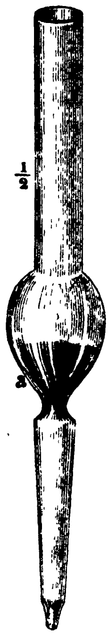

Fig. 69.

§ 48.

γ. SEPARATION OF PRECIPITATES BY DECANTATION AND FILTRATION COMBINED.

In the case of precipitates which, from their gelatinous nature, or from the firm adhesion of certain coprecipitated salts, cannot be well washed on the filter, the following method is resorted to. Let the precipitate subside as far as practicable, pour the nearly clear supernatant liquid on the filter, stir the precipitate up with the washing fluid (in certain cases, where such a course is indicated, heat to boiling), let it subside again, and repeat this operation until the precipitate is almost thoroughly washed. Transfer it now to the filter, and complete the operation with the washing-bottle (see § 46). This method is highly to be recommended where the precipitate is perfectly insoluble in the fluid used for washing; there are many precipitates that can be thoroughly washed only by its application.

In cases where it is not intended to weigh a precipitate washed by decantation, but to dissolve it again, the operation of washing is entirely completed by decantation, and the precipitate not even transferred to the filter. The re-solution of the bulk of the precipitate being effected in the vessel containing it, the filter is placed over the latter, and the solvent passed through it.

Although the termination of the operation of washing may be usually ascertained, by testing a sample of the washings for one of the substances originally present in the solution which has to be removed (for hydrochloric acid, for instance, with nitrate of silver), still there are cases in which this mode of proceeding is inapplicable. In such cases, and indeed in processes of washing by decantation generally, **Bunsen's** method will be found convenient—viz., to continue the process of washing until the fluid which remained in the beaker, after the first decantation, has been diluted ten thousand times. To effect this, measure with a slip of paper the height from the bottom of the beaker to the surface of the fluid remaining in it, together with the precipitate, after the first decantation; then fill the beaker with water, if possible, boiling, and measure the entire height of the fluid; divide the length of the second column by that of the first. Go through the same process each time you add fresh water, and always multiply the quotient found with the number obtained in the preceding calculation, until you reach 10000.

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* Zeitschr. f. anal. Chem. 8, 154.

† SILLIMAN'S American Journal (ii.), 44, 215.

§ 49.

Further Treatment of Precipitates.

Before proceeding to weigh a precipitate, it still remains to convert it into a form of accurately known composition. This is done either by igniting or by drying. The latter proceeding is more protracted and tedious than the former, and is, moreover, apt to give less accurate results. The process of drying is, therefore, as a general rule, applied only to precipitates which cannot bear exposure to a red heat without undergoing total or partial volatilization; or whose residues left upon ignition have no constant composition; thus, for instance, drying is resorted to for sulphide of mercury, sulphide of arsenic, and other metallic sulphides, and also for cyanide of silver, double chloride of platinum and potassium, &c. But whenever the nature of the precipitate (*e.g.*, sulphate of baryta, sulphate of lead, and many other compounds) leaves the operator at liberty to choose between drying and heating to redness, the latter process is almost invariably preferred.

§ 50.

aa. Drying of Precipitates.

When a precipitate has been collected, washed, and dried on a filter, minute particles of it adhere so firmly to the paper that it is found impossible to remove them. The weighing of dried precipitates involves, therefore, in all accurate analyses, the drying and weighing of the filter also. Formerly, chemists used two filters of equal size, the one placed within the other; after the precipitate had been dried, the outer filter was taken off, and placed on the balance as a counterpoise to the inner filter, which contained the precipitate. It was at the time assumed that filters of equal size were likewise of equal weight. This assumption, however, is inadmissible in accurate analyses, since every experiment shows that even small filters, of equal size, differ in weight to the extent of twenty, thirty, and even more milligrammes. To obtain accurate results, it is necessary to dry and weigh the filter before using it; the temperature at which the filter is dried must be the same as that to which it is intended subsequently to expose the precipitate. Another condition is that the filtering-paper must not contain any substance liable to be dissolved by the fluid passing through it.

The drying is conducted either in the water-, air-, or oil-bath, according to the degree of heat required. The weighing is performed in a closed vessel, mostly between two clasped watch-glasses (fig. 70), or in two tubes placed one within the other as shown in fig. 71, or in a platinum crucible. When the filter appears dry, it is placed between the warm watch-glasses, or in the tubes, or in the warm crucible, allowed to cool under a bell-glass, over sulphuric acid, and weighed. The reopened watch-glasses, tubes or crucible, together with the filter, are then again exposed for some time to the required degree of heat, and, after cooling, weighed once more. If the weight does not differ from that found at first, the filter may be considered dry, and we have simply to note the collective weight of the watch-glasses, clasp, and filter, or of the tubes and filter, or of the crucible and filter.

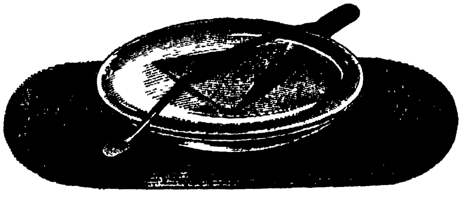
Fig. 70.

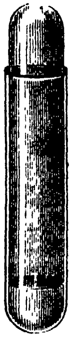
Fig. 71.

After the washing of the precipitate has been concluded, and the water allowed to run off as far as possible, the filter with the precipitate is taken off the funnel, folded up, and placed upon blotting-paper, which is then kept for some time in a moderately warm place, protected from dust; it is finally put into one of the watch-glasses, or into the narrower of the two tubes, or into the uncovered platinum crucible, with which it was first weighed, and exposed to the appropriate degree of heat, either in the water-, air-, or oil-bath. When it is judged that the precipitate is dry, the second watch-glass or the other tube or the lid of the crucible is put on (with the clasp pushed over the two in the first case), and the whole, after cooling in the desiccator, is weighed. The filter and the precipitate are then again exposed, in the same way, to the proper drying temperature, allowed to cool, and weighed again, the same process being repeated until the weight remains constant or varies only to the extent of a few deci-milligrammes. By subtracting from the weight found the tare of the containing vessel and filter, we obtain the weight of the dry precipitate.

It happens sometimes that the precipitate nearly fills the filter, or retains a considerable amount of water; or sometimes the paper is so thin that it cannot be removed from the funnel. In all such cases, the best way is to let the filter and precipitate get nearly dry in the funnel, by covering the latter with a piece of blotting-paper to keep out the dust, and placing it, supported on a broken beaker (fig. 72), or some other vessel of the kind, on the steam-

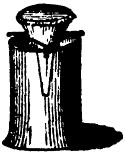
Fig. 72.

apparatus or sand-bath, or stove, or on a heated iron plate. For supports for funnels while drying I can recommend the little device, fig. 73. It consists of a hollow frustum of a cone open both ends, made of stoneware or tin plate. Two sizes may be used, 10 cm. and 12 cm. high respectively. The lower diameter should be from 7 to 8, the upper from 4 to 6 cm.

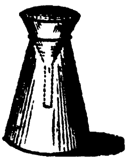
Fig. 73.

§ 51.

bb. Ignition of Precipitates.

It was customary formerly, in this process, to dry the precipitate with the filter, then to scrape the latter clean and remove it, previously to heating the precipitate to redness. This proceeding was inevitably attended with the loss of the minute particles which, however clean the filter may be scraped, will always adhere to it. Experience has shown that more accurate results are obtained if the filter is burned when the precipitate is ignited, and the weight of the filter ash subtracted from the weight found.

If care be taken to make the filters always of the same paper, and to cut every size by a pattern, the quantity of ash which each size yields upon incineration may be readily determined. It is necessary, however, to determine separately the quantity of ash left by ordinary filters, and that left by filters which have been washed with hydrochloric acid and water; on an average the latter leave about half as much ash as the former. To determine the filter ash take ten filters (or an equal weight of cuttings from the same paper), burn them in an obliquely-placed platinum crucible, and ignite until every trace of carbon is consumed; then weigh the ash, and divide the amount found by ten; the quotient expresses, with sufficient precision, the average quantity of ash which each filter leaves upon incineration.

In the ignition of precipitates, the following four points have to be more particularly regarded:

1. No loss of substance must be incurred;
2. The ignited precipitates must really be the bodies they are represented to be in the calculation of the results;
3. The incineration of the filters must be complete;
4. The crucibles must not be attacked.

The following two methods seem to me the simplest and most appropriate of all that have as yet been proposed. The selection of either depends upon certain circumstances, which I shall immediately have occasion to point out. But no matter which method is resorted to, the precipitate must always be thoroughly dried, before it can properly be exposed to a red heat. The application of a red heat to moist precipitates, more particularly to such as are very light and loose in the dry state (silicic acid, for instance), involves always a risk of loss from the impetuously escaping aqueous vapors carrying away with them minute particles of the substance. Some other substances, as hydrated sesquioxide of iron, for instance, form small hard lumps; if such lumps are ignited while still moist within they are liable to fly about with great violence. The best method of drying precipitates as a preliminary to ignition is as described in § 50, the last paragraph. When a precipitate has been washed by suction it may often be ignited at once with the filter—without any more drying.

Respecting the ignition, the degree of heat to be applied, and the duration of the process must, of course, depend upon the nature of the precipitate and upon its deportment at a red heat. As a general rule, a moderate red heat, applied for about five minutes, is found sufficient to effect the purpose ; there are, however, many exceptions to this rule which will be indicated wherever they occur.

Whenever the choice is permitted between porcelain and platinum crucibles, the latter are always preferred, on account of their comparative lightness and infrangibility, and because they are more readily heated to redness. The crucible selected should always be of sufficient capacity, as the use of crucibles deficient in size involves the risk of loss of substance. The proper size, in most cases, is 4 cm. in height, and 3·5 cm. in diameter. That the crucible must be perfectly clean, both inside and outside, need hardly be mentioned. The analyst should acquire the habit of cleaning and polishing the platinum crucible always after using it. This should be done as recommended by BERZELIUS, and lately also by ERDMANN, by friction with moist sea-sand whose grains are all round and do not scratch. I have found this method to answer extremely well. The sand is rubbed on with the finger, and the desired effect is produced in a few minutes. The adoption of this habit is attended with the pleasure of always working with a bright crucible and the profit of prolonging its existence. This mode of cleaning is all the more necessary, when one ignites over gas-lamps, since at this high temperature crucibles soon acquire a grey coating, which arises from a superficial loosening of the platinum. A little scouring with sea-sand readily removes the appearance in question, without causing any notable diminution of the weight of the crucible (ERDMANN*). If there are spots on the platinum crucibles, which cannot be removed by the sand without wearing away too much of the metal, a little bisulphate of potassa is fused in the crucible, the fluid mass shaken about inside, allowed to cool, and the crucible finally boiled with water. There are two ways of cleaning crucibles soiled outside ; either the crucible is placed in a larger one, and the interspace filled with bisulphate of potassa, which is then heated to fusion ; or the crucible is placed on a platinum-wire triangle, heated to redness, and then sprinkled over with powdered bisulphate of potassa. Instead of the bisulphate you may use borax. Never forget at last to polish the crucible with sea-sand again.

When the crucible is clean, it is placed upon a clean platinum-wire triangle (fig. 74), ignited, allowed to cool in the desiccator, and weighed. This operation, though not indispensable, is still always advisable, that the weighing of the empty and the filled crucible may be performed under as nearly as possible the same circumstances. The empty crucible may of course be weighed after the ignition of the precipitate; however, it is preferable in most cases to weigh it before. The weighing of the crucible after ignition of the

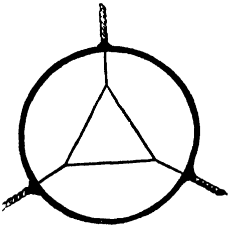

Fig. 74.

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* Journ. f. prakt. Chem. 79, 117.

precipitate is only necessary when the gas blowpipe has been used, which, as experience has shown, often reduces the weight of a platinum crucible.* In default of a platinum triangle, you may use an iron triangle, covering the part with which the crucible comes in contact with platinum-wire or foil, or pieces of tobacco pipe. The ignition is effected with a BERZELIUS spirit-lamp or a gas-lamp, or else in a muffle. If a BUNSEN's gas-lamp is used, the perforated porcelain plate is previously put on. The 6 spikes (see fig. 46) are provided for its support. In igniting reducible substances over lamps, the analyst must always be on his guard against the contact of unconsumed hydrocarbons even in covered crucibles. When gas-lamps are used there is especial need of caution in this respect. Reduction will be avoided if the flame is made no larger than necessary, if a chimney is used, if the crucible is supported in the upper part of the flame, and if, when the crucible is in a slanting position, it is heated from behind.

We pass on now to the description of the special methods.

§ 52.

FIRST METHOD. (*Ignition of the Precipitate with the Filter.*)

This method is resorted to in cases where there is no danger of a reduction of the precipitate by the action of the carbon of the filter. The mode of proceeding is as follows:—

The perfectly dry filter, with the precipitate, is removed from the funnel, and its sides are gathered together at the top, so that the precipitate lies enclosed as in a small bag. The filter is now put into the crucible, which is then covered and heated over a spirit-lamp with double draught or over gas very gently, to effect the slow charring of the filter; the cover is now removed, the crucible placed obliquely, and a stronger degree of heat applied, until complete incineration of the filter is effected; the lid, which had in the meantime best be kept in a porcelain dish, or in a porcelain crucible, is put on again, and a red heat applied for some time longer, if needed; the crucible is now allowed to cool a little, and is then, while still hot, though no longer red hot,† taken off with a pair of tongs of brass or polished iron (figs. 75 and 76), and put in the desiccator, where it is left to cool; it is finally weighed.

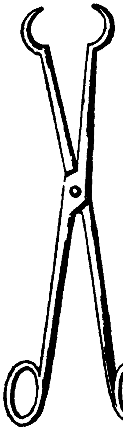

Fig. 75.

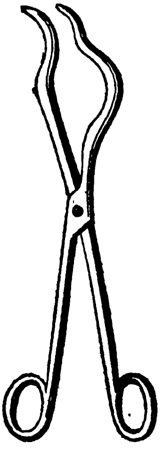

Fig. 76.

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* WITTSTEIN says that platinum crucibles do not lose weight on ignition, unless they contain small quantities of osmium (Zeitschr. f. anal. Chem. 5, 98). STOLBA ascribes the loss of weight to the formation of carbide of platinum. He says, that the rougher the surface the greater is the loss (Polyt. Journ. 198, 177).

† Taking hold of a *red-hot* crucible with brass tongs might cause the formation of black rings round it.

The combustion of the carbon of the filter may be promoted, in cases where it proceeds too slowly, by pushing the non-consumed particles, with a smooth and rather stout platinum-wire, within the focus of the strongest action of the heat and air. And the operator may also increase the draught of air by leaning the lid of the crucible against the latter in the manner illustrated in fig. 77.

It will occasionally happen that particles of the carbon of the filter obstinately resist incineration. In such cases the operation may be promoted by igniting for a short time over the blowpipe, or by putting a small lump of fused, dry nitrate of ammonia into the crucible, placing on the lid and applying a gentle heat at first, which is gradually increased. However, as this latter method is apt to involve some loss of substance, its application should not be made a general rule.

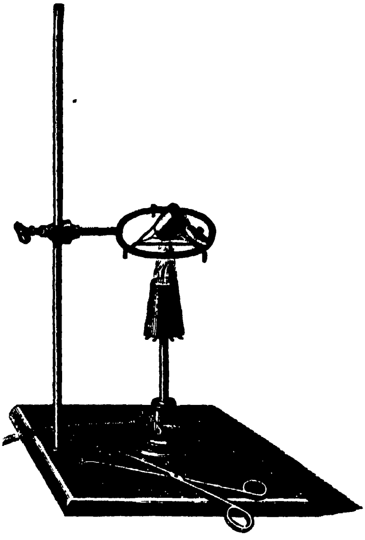

Fig. 77.

In cases where the bulk of the precipitate is easily detached from the filter, the preceding method is occasionally modified in this, that the precipitate is put into the crucible, and the filter, with the still adhering particles, folded loosely together, and laid over the precipitate. In other respects, the operation is conducted in the manner above described.

As above mentioned, precipitates which have been washed by suction may often be ignited immediately without further drying (Bunsen),* but, of course, this applies only to precipitates which are not liable to reduction by the carbon of the filter. We proceed thus: the clean half of the filter is folded round the half containing the precipitate four or five times; this is placed in a crucible fixed in a slanting position, and pressed with the finger against the interior of the crucible; the cover is supported as represented in fig. 77, and heat is first applied where the cover touches the top of the crucible. The heat is to be regulated that the carbonization may go on quietly without flame or much smoke. When the carbonization slackens, shift the lamp towards the bottom of the crucible. As soon as the filter is reduced to a charred mass of the original form, the crucible is made red hot till the carbon is burnt off, and the filter is converted into a white ash. If necessary you may ignite for a short time over the blowpipe.

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* Ann. d. Chem. u. Pharm. 148, 285; also Zeitschr. f. anal. Chem. 8, 186. In the case of alumina, Al. Mitscherlich had previously recommended the ignition of the moist precipitate (Zeitschr. f. anal. Chem. 1, 67).

§ 53.

Second Method. (*Ignition of the Precipitate apart from the Filter.*)

This method is resorted to in cases where a reduction of the precipitate from the action of the carbon of the filter is apprehended; and also where the ignited precipitate is required for further examination, which the presence of the filter ash might embarrass. It may be employed also, instead of the first method, in all cases where the precipitate is easily detached from the filter. The mode of proceeding is as follows:—

The crucible intended to receive the precipitate is placed upon a sheet of glazed paper; the perfectly dry filter with the precipitate is taken out of the funnel, and gently pressed together over the paper, to detach the precipitate from the filter; the precipitate is now shaken into the crucible, and the particles still adhering to the filter are removed from it, as far as practicable, by further pressing or gentle rubbing together of the folded filter, and are then also transferred to the crucible. The filter is cut up over the glazed paper with a pair of clean scissors into eight or ten pieces, the lid of the crucible is brought to redness, and one after another of the pieces is placed on the lid with the tongs, and allowed to burn, the lid being afterwards ignited till the last trace of carbon is consumed. If the lid is large and the filter small, the latter is not cut up, but merely folded. The lid is now laid on a porcelain crucible, and covered with a beaker. Finally, the crucible with the precipitate is ignited (if necessary another lid being placed on it), the lid containing the filter ash is put on towards the end, the crucible is allowed to cool a little, transferred to the desiccator, and weighed when cold.

With precipitates which are not absolutely insoluble in water (phosphate of magnesia and ammonia, for instance), a considerable time is often required to effect complete incineration, as the filter is saturated with a dilute solution of the precipitate. The incineration may be promoted by pressing the blackened filter against the red hot lid by means of a smooth wire or thin platinum knife. However, a certain amount of patience is always requisite in this operation.

With precipitates which on reduction do not yield bodies that combine with platinum, the following method of incinerating the filter, proposed by Bunsen, may also be employed. The filter being cleaned as much as possible is spread open upon the sheet of glazed paper, and then folded in form of a little square box, enclosed on all sides by the parts turned up; any minute particles of the precipitate that may have dropped on the glazed paper are brushed into this little box, with the aid of a small feather; the box is closed again, rolled up, and one end of a long platinum-wire spirally wound round it. The crucible being placed on or above a porcelain plate, the little roll is lighted, and, during its combustion, held over the crucible, so that the falling particles of the precipitate or filter ash may drop into it, or, at least, into the porcelain plate. In this way, and by occasionally holding the little roll again in or against the flame, the incineration of the filter is readily and safely effected. When the operation is terminated, a slight tap will suffice to drop the ash and the remaining particles of the precipitate into the crucible, which is then covered, and the ignition completed as in § 52. Where it is intended to keep the ash separate from the precipitate, it is made to drop into the lid of the crucible, in which case it is better to ignite the crucible with the principal portion of the precipitate first. If this method of incinerating the filter were adopted with such precipitates as chloride of silver or carbonate of lead, a small quantity of the metal would be reduced and alloy with the platinum-wire.

No matter which method of incineration is resorted to, the operation must always be conducted in a spot entirely protected from draughts.

Certain precipitates suffer some essential modification in their properties, in their solubility, for instance, from ignition. In cases where a portion of a substance of the kind is required, after weighing, for some other purpose in the unignited state, the two operations of drying and igniting may be combined in the following way:—The precipitate is collected on a filter dried at 100°; it is then also dried at 100°, and weighed (§ 50). A portion of the dry precipitate is put into a tared crucible, and its exact weight ascertained; it is then ignited and weighed again; the loss of weight is calculated on the whole amount of the precipitate.

§ 54.

5. VOLUMETRIC ANALYSIS.

The principle of volumetric analysis has been explained already in the Introduction, where we have seen how the quantity of protoxide of iron present in a fluid may be determined by means of a solution of permanganate of potassa, the value of which has been previously ascertained by observing the quantity required to oxidize a known amount of protoxide of iron.

In order to make the matter as clear as possible I will here adduce a few more examples.

Suppose we have prepared a solution of chloride of sodium of such a strength that 100 c.c. will exactly precipitate 1 grm. silver from its solution in nitric acid, we can use it to estimate unknown quantities of silver. Say, for instance, we have an alloy of silver and copper in unknown proportion, we dissolve 1 grm. in nitric acid, and add to the solution our solution of chloride of sodium, drop by drop, until the whole of the silver is thrown down, and an additional drop fails to produce a further precipitate. The amount of silver present may now be calculated from the amount of solution of chloride of sodium used. Thus, supposing we have used 80 c.c., the amount of silver present in the alloy is 80 per cent.; since, as 100 c.c. of the solution of chloride of sodium will throw down 1 grm. of pure silver (*i.e.* of 100 per cent.), it follows that every c.c. of the chloride of sodium solution corresponds to 1 per cent. of silver.

Another example. It is well known that iodine and sulphuretted hydrogen cannot exist together: whenever these two substances are brought in contact, decomposition immediately ensues, the hydrogen separating from the sulphur and combining with the iodine ($I + HS = HI + S$). Hydriodic acid exercises no action on starch-paste, whereas the least trace of free iodine colors it blue. Now, if we prepare a solution of iodine (in iodide of potassium) containing in 100 c.c. ·7462 grm. iodine, we may with this decompose exactly ·1 grm. sulphuretted hydrogen for 17 : 126·85 :: ·1 : ·7462. Let us suppose, then, we have before us a fluid containing an unknown amount of sulphuretted hydrogen, which it is our intention to determine. We add to it a little starch-paste, and then, drop by drop, our solution of iodine, until a persistent blue coloration of the fluid indicates the formation of iodide of starch, and hence the complete decomposition of the sulphuretted hydrogen. The amount of the latter originally present in the fluid may now be readily calculated from the amount of solution of iodine used. Say, for instance, we have used 50 c.c. of iodine solution, the fluid contained originally ·05 sulphuretted hydrogen; since, as we have seen, 100 c.c. of our iodine solution will decompose exactly ·1 grm. of that body.

Solutions of accurately known composition or strength, used for the purposes of volumetric analysis, are called *standard solutions.* They may be prepared in two ways, viz., (*a*) by dissolving a weighed quantity of a substance in a definite volume of fluid: or (*b*), by first preparing a suitably concentrated solution of the reagent required, and then determining its exact strength by a series of experiments made with it upon weighed quantities of the body for the determination of which it is intended to be used.

In the preparation of standard solutions by method *a*, a certain definite strength is adopted once for all, which is usually based upon the principle of an exact correspondence between the number of grammes of the reagent contained in a litre of the fluid, and the equivalent number of the reagent (H = 1). In the case of standard solutions prepared by method *b*, this may also be easily done, by diluting to the required degree the still somewhat too concentrated solution, after having accurately determined its strength; however, as a rule, this latter process is only resorted to in technical analyses, where it is desirable to avoid all calculation. Fluids which contain the eq. number of grammes of a substance in 1 litre, are called *normal solutions;* those which contain $\frac{1}{10}$ of this quantity, *decinormal solutions.*

The determination, or *titration*,* of a standard solution is obviously a most important operation; since any error in this will, of course, necessarily falsify every analysis made with it. In scientific and accurate researches it is, therefore, always advisable, whenever practicable, to examine the standard solution—no matter whether prepared by method *a*, or by method *b*, with subsequent dilution to the required degree—by experimenting with it upon accurately weighed quantities of the body for the determination of which it is to be used.

In the previous remarks I have made no difference between fluids of known composition and those of known power; and this has hitherto been usual. But by accepting the two expressions as synonymous, we take for granted that a fluid exercises a chemical action exactly corresponding to the amount of dissolved substance it contains—that, for instance, a solution of chloride of sodium containing 1 eq. NaCl will precipitate exactly 1 eq. silver. This presumption, however, is very often not absolutely correct, as will be shown with reference to this very example, § 115, *b*, 5. In such cases, of course, it is not merely advisable, but even absolutely necessary, to determine the strength of the fluid by experiment, although the amount of the reagent it contains may be exactly known, for the power of the fluid can be inferred from its composition only approximately and not with perfect exactness.

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* From *titre*, French for the amount of gold or silver in coin.

If a standard solution keeps unaltered, this is a great advantage, as it dispenses with the necessity of determining its strength before every fresh analysis.

That particular change in the fluid operated upon by means of a standard solution which marks the completion of the intended decomposition, is termed the FINAL REACTION. This consists either in a *change of color*, as when a solution of permanganate of potassa acts upon an acidified solution of protoxide of iron, or a solution of iodine upon a solution of sulphuretted hydrogen mixed with starch-paste; or in the *cessation of the formation of a precipitate* upon further addition of the standard solution, as when a standard solution of chloride of sodium is used to precipitate silver from its solution in nitric acid; or in *incipient precipitation*, as when a standard solution of silver is added to a solution of hydrocyanic acid mixed with an alkali; or in *a change in the action of the examined fluid upon a particular reagent*, as when a solution of arsenite of soda is added to a solution of chloride of lime, until the mixture no longer imparts a blue tint to paper saturated with iodide of potassium and starch-paste.

The more sensitive a final reaction is, and the more readily, positively, and rapidly it manifests itself, the better is it calculated to serve as the basis of a volumetric method. In cases where it is desired to ascertain with the greatest precision the moment when the reaction is completed, the analyst may sometimes prepare, besides the actual standard solution, another, ten times more dilute, and use the latter to finish the process, carried nearly to completion with the former.

But a good final reaction is not of itself sufficient to afford a safe basis for a good volumetric method; this requires, as the first and most indispensable condition, that the particular decomposition which constitutes the leading point of the analytical process should—at least under certain known circumstances—remain unalterably the same. Wherever this is not the case—where the action varies with the concentration of the fluid, or with the free acid present, or with the rate of action of the standard solution, or where a precipitate formed in the course of the process has not the same composition throughout the operation—the basis of the volumetric method is fallacious, and the method itself of no value.

When the new system of volumetric analysis first began to find favor with chemists, a great many volumetric methods were proposed, based simply upon some final reaction, without a careful study of the decomposition involved; the result was a superabundant crop of new volumetric methods, of which a great many were useless. All the methods, however, have been subjected to a sifting process, more particularly by the hands of F. MOHR; and in the special part of the present work I have taken care to separate the really good methods from the fallacious.

SECTION II.

REAGENTS.

§ 55.

For general information respecting reagents, I refer the student to the "Qualitative Analysis."

The instructions given here will be confined to the preparation, testing, and most important uses of those substances which subserve principally and more exclusively the purposes of quantitative analysis. Those reagents which are employed in qualitative investigations, will be simply mentioned here by name.

The reagents used in quantitative analysis, are properly arranged under the following heads :—

A. Reagents for gravimetric analysis in the wet way.
B. Reagents for gravimetric analysis in the dry way.
C. Reagents for volumetric analysis.
D. Reagents used in organic analysis.

The mode of preparing the fluids used in volumetric analysis, the reagents used only in special cases, and the absorption bulbs used in gas analysis, will be found where we shall have occasion to speak of their application.

A. REAGENTS FOR GRAVIMETRIC ANALYSIS IN THE WET WAY.

I. SIMPLE SOLVENTS.

§ 56.

1. **Distilled Water** (see "Qual. Anal.").

Water intended for quantitative investigations must be perfectly pure. Water distilled from glass vessels leaves a residue upon evaporation in a platinum vessel (see Experiment No. 5), and is therefore inapplicable for many purposes; as for instance, for the determination of the solubility of sparingly soluble substances. For certain uses it is necessary to free the water by ebullition from atmospheric air and carbonic acid.

2. **Alcohol** (see "Qual. Anal.").

a. Absolute alcohol. *b.* Rectified spirit of wine of various degrees of strength.

3. **Ether.**

The application of ether as a solvent is very limited. It is more frequently used mixed with spirit of wine, in order to diminish the solvent power of the latter for certain substances, *e.g.*, bichloride of platinum and chloride of ammonium. Commercial ether will answer the purpose.

4. Bisulphide of Carbon.

This should be purified, if necessary, by shaking with mercury, which removes its usual unpleasant odor, and rectifying over a water-bath. No india-rubber connexions must be used in the latter operation. Bisulphide of carbon is used to dissolve and separate iodine from aqueous solutions, and to free sulphides of metals from admixed sulphur.

II. ACIDS AND HALOGENS.

a. Oxygen Acids.

§ 57.

1. Sulphuric Acid.

a. Concentrated commercial sulphuric acid.
b. Concentrated pure sulphuric acid.
c. Dilute sulphuric acid.
See "Qual. Anal."

2. Nitric Acid.

a. Pure nitric acid of 1·2 sp. gr. (see "Qual. Anal.").

b. Red fuming nitric acid (concentrated nitric acid containing hyponitric acid).

Preparation.—Mix 1000 grm. pure nitrate of potassa with 15 grm. starch in lumps, put the mixture into a capacious tubulated retort, and add 500 grm. sulphuric acid, and 500 grm. Nordhausen sulphuric acid. Place the retort on a wire-gauze, over a gas or on a sand-bath. The distillation will commence without the application of heat. If the nitre was not quite free from chlorides, collect the first portions of the distillate separately. When the drops come over slowly, heat gently, but by no means push on the operation too quickly. As soon as no more acid comes off at a moderate heat, the operation will be completed. As a part of the hyponitric acid is sure to escape, the distillation should be conducted in the open air, or under a good draught.

Tests.—Red fuming nitric acid must be in a state of the greatest possible concentration, and perfectly free from sulphuric acid. In order to detect minute traces of the latter, evaporate a few c.c. in a porcelain dish nearly to dryness, dilute the residue with water, add some chloride of barium, and observe whether a precipitate forms on standing.

Uses.—A powerful oxidizing agent and solvent; it serves more especially to convert sulphur and metallic sulphides into sulphuric acid and sulphates respectively.

3. Acetic Acid (see "Qual. Anal.").

4. Tartaric Acid (see "Qual. Anal.").

γ. *Heavy Metals, and their Oxides.*

§ 60.

1. Zinc.

Zinc has of late been much used in quantitative analysis. It serves more especially to effect the reduction of dissolved sesquioxide of iron to protoxide, and also the precipitation of copper. Zinc intended to be used for the former purpose must be free from iron, for the latter free from lead, copper, and other metals which remain undissolved upon treating the zinc with dilute acids. As it is not easy to prepare zinc which answers both purposes in any quantity, it is well to keep besides the ordinary zinc for hydrogen preparation also the two following kinds :

a. Zinc free from iron.—The distillation of zinc in the laboratory being a troublesome and costly operation, chemists generally use the raw product of the reduction and distillation of the ore, as this contains, at least in many cases, only such trifling traces of iron that it may be safely used for reducing solutions of sesquioxide of iron. The ordinary zinc of commerce, which is prepared by fusing the reduced metal in iron pots, contains much more iron. Of the several sorts of crude zinc which I have had occasion to examine, Silesian zinc contains the least admixture of iron.

b. Zinc free from lead, copper, &c.—To procure zinc which leaves no residue upon solution in dilute sulphuric acid, there is no other resource but to re-distil the commercial article.

This is effected in a retort made of the material of Hessian or black lead crucibles. The operation is conducted in a wind furnace with good draught. The neck of the retort must hang down as perpendicularly as possible. Over this is placed a small drain-pipe, the lower end of which is allowed just to dip into water contained in a tub, or large stoneware dish; the joints are stopped up with clay. The distillation begins as soon as the retort is at a bright red heat. As the neck of the retort is very liable to become choked up with oxide of zinc, it is necessary to keep it constantly free by means of a piece of iron wire. The zinc obtained by this re-distillation is as good as free from lead, but it still contains perceptible traces of iron (from the wire). If the total absence of iron in the product is desired, we must use the stem of a clay pipe or a stick instead of the iron wire.

Tests.—The following is the simplest way of testing the purity of zinc: dissolve the metal in dilute sulphuric acid in a small flask provided with a gas-evolution tube, place the outer limb of the tube under water, and when the solution is completed, let the water entirely or partly recede into the flask; after cooling, add to the fluid, drop by drop, a sufficiently dilute solution of permanganate of potassa. If a drop of that solution imparts the same red tint to the zinc solution as to an equal volume of acidulated water, the zinc may be considered free from iron. I prefer this way of testing the purity of zinc to other methods, as it affords, at the same time, an approximate, or, if the zinc has been weighed, and the permanganate solution (which, in that case, must be considerably diluted) measured, an accurate knowledge of the quantity of iron present. If lead or copper is present, it will remain undissolved upon solution of the zinc.

2. COPPER.

The copper of commerce, with the exception of the Japanese, is rarely sufficiently pure for analytical purposes. The chemist may prepare this metal for himself in a state of purity, either in the galvanoplastic way, or as follows: precipitate the metal from a solution of the sulphate by a clean iron plate, free the precipitated copper from iron by boiling with hydrochloric acid; wash, dry, fuse, and roll into thin sheets (FUCHS).

Tests.—Pure copper must dissolve completely in nitric acid, and addition of ammonia in excess to this solution must not, even after long standing, produce in it any precipitate (iron, lead, &c.); neither should the addition of hydrochloric acid render the solution turbid (silver). If its solution be precipitated with sulphuretted hydrogen, the filtrate should leave no residue on evaporation.

Uses.—This metal serves us occasionally in indirect analysis; thus it is used, for instance, to determine copper, also iron according to FUCHS, &c. However, since the introduction of volumetric methods, it is but rarely used in quantitative analysis.

3. OXIDE OF LEAD.

Precipitate pure nitrate or acetate of lead with carbonate of ammonia, wash the precipitate, dry and ignite gently to complete decomposition.

Oxide of lead is often used to fix an acid, so that it is not expelled even by a red heat.

4. OXIDE OF MERCURY.

Preparation.—Pour a solution of chloride of mercury into a hot moderately dilute solution of soda, taking care to leave the solution of soda always in excess, and wash the yellow precipitate thoroughly by decantation; lastly mix with water, and keep in a bottle in this condition.

Tests.—Oxide of mercury must leave no residue when heated to redness in a platinum crucible.

Uses.—This reagent serves, in quantitative investigations, principally to decompose chloride of magnesium in the process of separating magnesia from the alkalies.

b. Sulphur Bases.

1. SULPHIDE OF AMMONIUM (see "Qual. Anal.").

We require both the colorless monosulphide, and the yellow polysulphide.

2. SULPHIDE OF SODIUM (see "Qual. Anal.").

IV. SALTS.

a. Salts of the Alkalies.

§ 61.

1. SULPHATE OF POTASSA (see "Qual. Anal.").

2. PHOSPHATE OF AMMONIA.

Preparation.—To pure dilute phosphoric acid (prepared from phosphorus) add pure ammonia to strongly alkaline reaction, allow to stand some time, filter, if necessary, and keep for use.

Tests.—Phosphate of ammonia must be free from arsenic, nitric, and sulphuric acids, but more particularly from potassa, or soda. The presence of either of these alkalies may be detected by adding solution of pure acetate of lead, until the formation of a precipitate ceases, filtering, precipitating the excess of lead with sulphuretted hydrogen, filtering again, evaporating to dryness, and igniting the residue. If there now remains a residue soluble in water, and of alkaline reaction, this may be considered a conclusive proof of the presence of soda or potassa.

In most cases phosphate of soda (see "Qual. Anal.") may be substituted for phosphate of ammonia.

3. Oxalate of Ammonia (see "Qual. Anal.").

4. Acetate of Soda (see "Qual. Anal.").

5. Succinate of Ammonia.

Preparation.—Purify succinic acid, by dissolving in nitric acid and recrystallizing, and then saturate it with dilute ammonia. The reaction should be rather slightly alkaline than acid.

Uses.—This reagent serves occasionally to separate sesquioxide of iron from other metallic oxides.

6. Carbonate of Soda (see "Qual. Anal.").

This reagent is required both in solution and in pure crystals; in the latter form to neutralize an excess of acid in a fluid which it is desirable not to dilute too much.

7. Carbonate of Ammonia (see "Qual. Anal.").

8. Bisulphite of Soda (see "Qual. Anal.").

9. Hyposulphite of Soda.

This salt occurs in commerce. It should be dry, clear, well crystallized, completely and with ease soluble in water. The solution must give with nitrate of silver at first a white precipitate, must not effervesce with acetic acid, and when acidified must give no precipitate with chloride of barium, or at most, only a slight turbidity. The acidified solution must, after a short time, become milky from separation of sulphur.

Uses.—The hyposulphite of soda is used for the precipitation of several metals, as sulphides, particularly in separations, for instance, of copper from zinc; it also serves as a solvent for several salts (chloride of silver, sulphate of lime, &c.); lastly, it is employed in volumetric analysis, its use here depending on the reaction $2 (NaO,S_2O_2) + I = NaI + NaO, S_4O_5$.

10. Nitrite of Potassa (see "Qual. Anal.").

11. Bichromate of Potassa (see "Qual. Anal.").

12. Molybdate of Ammonia (see "Qual. Anal.").

When this solution is used for estimating phosphoric acid, the filtrate from the phospho-molybdate of ammonia and that from the ammonia-phosphate of magnesia should be preserved. The molybdic acid may be recovered from these residues as follows. Evaporate the fluid in the open air or under a good draught to dryness, and finally heat till the greater part of the nitrate of ammonia is decomposed. Digest the residue with ammonia which dissolves the molybdic acid, and filter. Mix the filtrate with a little magnesia mixture (§ 62, 6) to precipitate any phosphoric acid. If a precipitate is formed, make sure that all the phosphoric acid is thrown down. Allow to stand some time, filter, add nitric acid till just acid, filter off the molybdic acid which separates by suction, and wash with the least quantity of water. The filtrate and washings from the molybdic acid contain but little acid. They may be worked up with the next lot of residues.

13. Chloride of Ammonium (see "Qual. Anal.").

14. Cyanide of Potassium (see "Qual. Anal.").

Besides the cyanide of potassium prepared by Liebig's method, which contains cyanate and carbonate of potassa, we require the pure salt in several cases of separation, for instance, in Wöhler's method of separating zinc and nickel. This is prepared as follows. Powder 2 parts of crystallized ferrocyanide of potassium, transfer to a retort and add 4 parts of water and 1½ of sulphuric acid. Now dissolve 1 part of potassa (evaporated till it will just solidify on cooling, not fused) in 3 or 4 parts of alcohol of at least 92 per cent., and filter; place the solution in the receiver, which should be kept cool. Apply heat to the retort and pass the hydrocyanic acid vapor into the potash, continuing the distillation till the residue begins to bump. The potash should remain in slight excess at the end of the operation. Filter the saline mass by suction, wash with a little alcohol, allow to drain thoroughly, dry in a porcelain dish and preserve in a well-closed bottle.

b. Salts of Alkaline Earths.

§ 62.

1. Chloride of Barium (see "Qual. Anal.").

The following process gives a very pure chloride of barium, free from lime and strontia :—Transmit through a concentrated solution of the impure salt hydrochloric gas, as long as a precipitate continues to form. Nearly the whole of the chloride of barium present is by this means separated from the solution, in form of a crystalline powder. Collect this on a filter, let the liquid drain off (it is best to apply suction), wash repeatedly with small quantities of pure hydrochloric acid, until a sample of the washings, diluted with water, and precipitated with sulphuric acid, gives a filtrate which, upon evaporation in a platinum dish, leaves no residue. The hydrochloric mother-liquor serves to dissolve fresh portions of witherite. I make use of the chloride of barium so obtained, principally for the preparation of perfectly pure carbonate of baryta, which is often required in quantitative analysis.

2. Acetate of Baryta.

Preparation.—Dissolve pure carbonate of baryta in moderately dilute acetic acid, filter, and evaporate to crystallization.

Tests.—Dilute solution of acetate of baryta must not be rendered turbid by nitrate of silver. See also *Chloride of barium.*

Uses.—Acetate of baryta is used instead of chloride of barium, to effect the precipitation of sulphuric acid, in cases where it is desirable to avoid the introduction of a chloride into the solution, or to convert the base into an acetate. As the reagent is seldom required, it is best kept in crystals.

3. Carbonate of Baryta (see "Qual. Anal.").

4. Chloride of Strontium.

Preparation.—Chloride of strontium is prepared from strontianite or celestine, by the same processes as chloride of barium. (See "Qual. Anal."). The pure crystals obtained are dissolved in spirit of wine of 96 per cent., the solution is filtered, and kept for use.

Uses.—The alcoholic solution of chloride of strontium is used to effect the conversion of alkaline sulphates into chlorides, where it is desirable to avoid the introduction into the fluid of a salt insoluble in spirit of wine.

5. Chloride of Calcium (see "Qual Anal.").

6. Sulphate of Magnesia (see " Qual. Anal.").

This reagent is principally used to precipitate phosphoric acid or arsenic acid from aqueous solutions. The solution required for this purpose should be kept ready prepared : it is made by dissolving 1 part of crystallized sulphate of magnesia and 2 parts of pure chloride of ammonium in 8 parts of water and 4 parts of solution of ammonia, allowing the fluid to stand at rest for several days, and then filtering. This solution is sometimes called magnesia-mixture.

c. Salts of the Oxides of the Heavy Metals.

§ 63.

1. Sulphate of Protoxide of Iron (see "Qual. Anal.").

2. Sesquichloride of Iron (see " Qual. Anal.").

3. Acetate of Sesquioxide of Uranium.

Heat finely powdered pitchblende with dilute nitric acid, filter the fluid from the undissolved portion, and treat the filtrate with hydrosulphuric acid, to remove the lead, copper, and arsenic; filter again, evaporate to dryness, extract the residue with water, and filter the solution from the oxides of iron, cobalt and manganese. Nitrate of sesquioxide of uranium crystallizes from the filtrate; purify this by recrystallization, and then heat the crystals until a small portion of the sesquioxide of uranium is reduced. Warm the yellowish-red mass thus obtained with acetic acid, filter and let the filtrate crystallize. The crystals are acetate of sesquioxide of uranium, and the mother-liquor contains the undecomposed nitrate (Wertheim). The salt may be still more conveniently prepared from the commercial compound of soda and sesquioxide of uranium,* as follows. Digest 1 part of this substance with 2 parts acetic acid of 1·038 sp. gr., then add 25 parts water, heat, filter, evaporate and crystallize. The uranium in the last mother-liquors may be precipitated by ammonia.

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* This may be obtained from the K.K. Bergoberamt, Joachimsthal.

Residues may be worked up as follows. Pour off the clear liquor from any deposit of phosphate of uranium and precipitate the uranium in it with phosphate of soda, wash the precipitate by decantation and add it to the deposit. Dissolve in hydrochloric acid, add sesquichloride of iron till a sample gives a brownish precipitate on addition of carbonate of ammonia, dilute and then add to the solution, which should contain a sufficient excess of hydrochloric acid, an excess of solution of common carbonate of soda. All the phosphoric acid will be thrown down as basic phosphate of sesquioxide of iron, the sesquioxide of uranium will remain in the solution which contains bicarbonate of soda. Filter, wash, acidify the filtrate with hydrochloric acid, heat till the carbonic acid is expelled and precipitate the sesquioxide of uranium in the heat by ammonia. Wash and dissolve in acetic acid (E. REICHARD*).

Tests.—Solution of acetate of sesquioxide of uranium after acidification with hydrochloric acid must not be altered by hydrosulphuric acid; carbonate of ammonia must produce in it a precipitate, soluble in an excess of the precipitant. A sample of the dilute solution should acquire a red tint when mixed with a little sulphuric acid and a drop of permanganate of potassa (absence of a salt of protoxide of uranium).

Uses.—Acetate of sesquioxide of uranium may serve, in many cases, to effect the separation and determination of phosphoric acid and arsenic acid.

4. NITRATE OF SILVER (see "Qual. Anal.").
5. ACETATE ON LEAD (see " Qual. Anal.").
6. CHLORIDE OF MERCURY (see " Qual. Anal.").
7. PROTOCHLORIDE OF TIN (see "Qual. Anal.").
8. BICHLORIDE OF PLATINUM (see " Qual. Anal.").

It is convenient to know approximately the strength of this solution. Let 10 or 20 c.c. contain 1 grm. platinum.

9. SODIO-PROTOCHLORIDE OF PALLADIUM (see "Qual. Anal.").

B. REAGENTS FOR GRAVIMETRIC ANALYSIS IN THE DRY WAY.

§ 64.

1. CARBONATE OF SODA, pure anhydrous (see "Qual. Anal.").
2. MIXED CARBONATES OF SODA AND POTASSA (see " Qual. Anal.").
3. HYDRATE OF BARYTA (see "Qual. Anal.").
4. NITRATE OF POTASSA (see " Qual. Anal.").
5. NITRATE OF SODA (see "Qual. Anal.").
6. BORAX (fused).

Preparation.—Heat crystallized borax (see " Qual. Anal.") in a platinum or porcelain dish, until there is no further intumescence; reduce the porous mass to powder, and heat this in a platinum crucible until it is fused to a transparent mass. If it is not required for immediate use, pour the semi-fluid, viscid mass upon a fragment of porcelain. A better way, in the latter case, is to fuse the borax on a piece of platinum gauze, by making the gas blowpipe-flame act upon it. The drops are collected in a platinum dish. The vitrified borax obtained is kept in a well-stoppered bottle. But as it is always necessary to heat the vitrified borax previous to use, to make quite sure that it is perfectly anhydrous, the best way is to prepare it only when required.

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* Zeitschr. f. anal. Chem. 8, 116.

Uses.—Vitrified borax is used to effect the expulsion of carbonic acid and other volatile acids, at a red heat.

7. Bisulphate of Potassa.

Preparation.—Mix 87 parts of neutral sulphate of potassa (see "Qual. Anal."), in a platinum crucible, with 49 parts of sulphuric acid, and heat to gentle redness, until the mass is in a state of calm fusion. Pour the fused salt on a fragment of porcelain, or into a platinum dish standing in cold water. After cooling, break the mass into pieces, and keep for use.

Uses.—This reagent serves as a flux for certain native compounds of alumina and sesquioxide of chromium. Bisulphate of potassa is used also, as we have already had occasion to state, for the cleansing of platinum crucibles; for this latter purpose, however, the salt which is obtained in the preparation of nitric acid, will be found sufficiently pure.

8. Bisulphate of Soda.

Preparation.—Like the previous salt, using 71 parts of pure sulphate of soda and 49 parts sulphuric acid.

Uses.—The bisulphate of soda serves the same purposes as the bisulphate of potassa, and is to be substituted for it when, as in the fusion of corundum, alum may crystallize out to the annoyance of the analyst (L. Smith*).

9. Fluoride of Potassium and Hydrogen.

Preparation.—Neutralize a definite quantity of hydrofluoric acid in a platinum dish with pure carbonate or hydrate of potassa, finally applying heat; then add a quantity of hydrofluoric acid equal to that first used, and evaporate to dryness. It is usual to prepare this substance immediately before it is required; if it is to be preserved, a gutta-percha vessel must be used.

Tests.—The following tests should produce no change—namely, sulphuretted hydrogen, ammonia, ammonia and sulphide of ammonium, carbonate of ammonia, and ammonia and phosphate of soda.

Uses.—This preparation is a valuable flux for many minerals which are usually considered very refractory, such as tinstone and chromic iron (Gibbs†).

10. Fluoride of Ammonium and Hydrogen.

Preparation.—To hydrofluoric acid or hydrofluosilicic acid, best in a platinum dish, add ammonia to strongly alkaline reaction, allow to stand for some time at a gentle heat, filter if necessary, and evaporate the filtrate in a platinum dish to dryness. Half the ammonia will escape, the above salt remaining behind. If it is to be preserved, a gutta-percha vessel must be used.

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* Zeitschr. f. anal. Chem. 4, 412.

† *Ib.* 3, 399.

Tests.—Like fluoride of potassium and hydrogen. Also a sample heated in platinum should leave no fixed residue. The last test should be applied in the open air or under a good draught.

Uses.—This preparation may be very advantageously substituted for hydrofluoric acid in the analysis of silicates.

11. CARBONATE OF AMMONIA (solid).

Preparation.—See "Qual. Anal."—This reagent serves to convert the bisulphates of the alkalies into neutral salts. It must completely volatilize when heated in a platinum dish.

12. NITRATE OF AMMONIA.

Preparation.—Neutralize pure carbonate of ammonia with pure nitric acid, warm, and add ammonia to slightly alkaline reaction; filter, if necessary, and let the filtrate crystallize. Fuse the crystals in a platinum dish, and pour the fused mass on a piece of porcelain; break into pieces whilst still warm, and keep in a well-stoppered bottle.

Tests.—Nitrate of ammonia must leave no residue when heated in a platinum dish.

Uses.—Nitrate of ammonia serves as an oxidizing agent; for instance, to convert lead into oxide of lead, or to effect the combustion of carbon, in cases where it is desired to avoid the use of fixed salts.

13. CHLORIDE OF AMMONIUM.

Preparation and Tests.—See "Qual. Anal."

Uses.—Chloride of ammonium is often used to convert metallic oxides and acids, *e.g.*, oxide of lead, oxide of zinc, binoxide of tin, arsenic acid, antimonic acid, &c. into chlorides (ammonia and water escape in the process). Many metallic chlorides being volatile, and others volatilizing in presence of chloride of ammonium fumes, they may be completely removed by igniting them with chloride of ammonium in excess, and thus many compounds, *e.g.*, alkaline antimonates, may be easily and expeditiously analysed. Chloride of ammonium is also used to convert various salts with other acids into chlorides, *e.g.*, small quantities of alkaline sulphates.

14. HYDROGEN GAS.

Preparation.—Hydrogen gas is produced by the action of dilute sulphuric acid on granulated zinc. It is best purified from traces of foreign gases by passing first through chloride of mercury solution, then through potash solution. If the gas is desired dry, pass through sulphuric acid or a chloride of calcium tube. If the hydrogen does not come off easily, add a drop of bichloride of platinum.

Tests.—Pure hydrogen gas is inodorous. It ought to burn from a platinum jet with a colorless, non-luminous flame, which, when cooled by depressing a porcelain dish upon it, must deposit nothing on the surface of the dish except pure water (free from acid reaction).

Uses.—Hydrogen gas is frequently used, in quantitative analysis, to reduce oxides, chlorides, sulphides, &c., to the metallic state, and also to protect certain bodies, such as metallic sulphides, from the atmosphere during ignition.

15. Chlorine.

Preparation.—See "Qual. Anal."—Chlorine gas is purified and dried by transmitting it through a U-tube containing fragments of binoxide of manganese, then through concentrated sulphuric acid, or a chloride of calcium tube.

Uses.—Chlorine gas serves principally to produce chlorides, and to separate the volatile from the non-volatile chlorides; it is also used to displace and indirectly determine bromine and iodine, and to convert lower chlorine compounds into higher.

C. REAGENTS USED IN VOLUMETRIC ANALYSIS.

§ 65.

Under this head are arranged the most important of those substances, which serve for the preparation and testing of the fluids required in volumetric analysis, and have not been given under *A* and *B*.

1. Pure Crystallized Oxalic Acid.

The introduction of crystallized oxalic acid as a basis for alkalimetry and acidimetry is due to Fr. Mohr. It is also employed to standardize a solution of permanganate of potassa, 1 equivalent of permanganic acid being required to convert 5 equivalents of oxalic acid* into carbonic acid ($Mn_2O_7 + 2\ SO_3 + 5\ C_2O_3 = 2\,(MnO,\ SO_3) + 10\ CO_2$). We use in most cases the pure crystallized acid which has the formula C_2O_3, HO + 2 aq., and whose equivalent is accordingly 63.

Preparation.—Treat powdered oxalic acid of commerce, in a flask, with lukewarm distilled water, in such proportion as will leave a large amount of the acid undissolved, and shake (Mohr). Filter, crystallize by rapid cooling, and let the crystals drain; then spread them out on blotting-paper, and let them get thoroughly dry, at the common temperature, in a place free from dust; or press them gently between sheets of blotting-paper, and repeat the operation with fresh sheets, until the crystals are quite dry.

Tests.—The crystals of oxalic acid must not show the least sign of efflorescence (to which they are liable even at 20° in a dry atmosphere); they must dissolve in water to a perfectly clear fluid; when heated in a platinum dish, they must leave no fixed and incombustible residue (carbonate of lime, carbonate of potassa, &c.). If the acid obtained by a first crystallization fails to satisfy these requirements, it must be recrystallized. In this case the strength of the solution should be so adjusted that not more than 10 or 20 per cent. of the acid may crystallize out at first; this crop will contain the foreign salts. Remove these crystals, and evaporate the mother-liquor further to obtain a second crop, consisting of the pure acid.

2. Tincture of Litmus.

Preparation.—Digest 1 part of litmus of commerce with 6 parts of water, on the water-bath, for some time, filter, divide the blue fluid into 2 portions, and saturate, in one-half the free alkali, by stirring repeatedly with a glass rod dipped in very dilute nitric acid, until the color just appears red; add the remaining blue half, together with 1 part of strong spirits of wine, and keep the tincture, which is now ready for use, in a small open bottle, not quite full, in a place protected from dust. In a stoppered bottle the tincture would speedily lose color.

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* Considered as a monobasic acid.

Tests.—Litmus tincture is tested by coloring with it about 100 c.c. of water distinctly blue, dividing the fluid into two portions, and adding to the one the least quantity of a dilute acid, to the other a trace of solution of soda. If the one portion acquires a distinct red, the other a distinct blue tint, the litmus tincture is fit for use, as neither acid nor alkali predominates.

3. PERMANGANATE OF POTASSA.

Preparation.—Mix 8 parts of very finely powdered pure pyrolusite, or the oxide of manganese left by gentle ignition of the carbonate, with 7 parts of chlorate of potassa, put the mixture into a shallow cast-iron pot, and add 37 parts of a solution of potassa of 1·27 sp. gr. (the same solution as is used in organic analysis*); evaporate to dryness, stirring the mixture during the operation; put the residue, before it has absorbed moisture, into an iron or Hessian crucible, and expose to a dull-red heat, with frequent stirring with an iron rod or iron spatula, until no more aqueous vapors escape, and the mass is in a faint glow. Remove the crucible now from the fire, and transfer the friable mass to an iron pot. Reduce to coarse powder, and transfer this, in small portions at a time, to an iron vessel containing 100 parts of boiling water; keep boiling, replacing the evaporating water, and passing a stream of carbonic acid through the fluid (MULDER). The originally dark-green solution of manganate of potassa soon changes, with separation of hydrated binoxide of manganese, to the deep violet-red of the permanganate. When it is considered that the conversion is complete, allow to settle, take out a small quantity of the clear liquid, boil and pass carbonic acid through it. If a precipitate forms the conversion is not yet complete.

The following method, recommended by STÄDELER,† is more rapid. After the fusion, reduce the product to powder, transfer to a flask, and macerate with an equal weight of cold water, then add the same quantity of water, and pass chlorine with frequent shaking till the color is a pure red. Dilute with four times its volume of water, and allow to settle. In this way the yield is increased by half, since no binoxide of manganese is thrown down. On the other hand, if the fused mass contains excess of potassa, chlorate of potassa may be formed, which will interfere with the purity of the crystals obtained.

When the red solution, prepared in one or other of the above ways, has been allowed to settle, pour it off, wash the deposit by decantation, mix the two fluids, evaporate over the fire to the crystallizing point, and allow to cool. The mother-liquor, if evaporated again, will yield another crop of crystals. A third crop cannot be obtained, as the liquor will contain too much chloride of potassium; it may be used for preparing binoxide of manganese. If the crystals are not pure enough, they may be recrystallized with ease. They are dried on a plate of plaster of Paris.

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* Or instead of the solution, use ten parts of the hydrate (K O, H O). In this case fuse the potash and the chlorate together first, and then project the manganese into the crucible.

† Journ. f. prakt. Chem. 103, 107.

If it is necessary to filter a solution of permanganate of potassa, this may be done through gun-cotton, asbestos, or previously ignited sand.

4. Ammonio-Sulphate of Protoxide of Iron.

$$(FeO,SO_3 + NH_4O,SO_3 + 6\,aq.)$$

Fr. Mohr has proposed to employ this double salt, which is scarcely liable to efflorescence and oxidation, as an agent to determine the strength of permanganate solution.

Preparation.—To two parts of water add one part of sulphuric acid, and divide into two equal portions. Warm one with a moderate excess of small iron nails free from rust, until the evolution of hydrogen gas has altogether or very nearly ceased. Warm the other portion, and add carbonate of ammonia in coarse powder till the fluid is neutral. Now add to the iron solution a few drops of dilute sulphuric acid, and filter it immediately. Filter the sulphate of ammonia if necessary, and add a few drops of dilute sulphuric acid. Mix the two warm filtrates in a porcelain dish, and stir till cold. Allow to stand some hours, collect the bluish-white powder in a funnel, remove the mother-liquor by suction, wash with a small quantity of spirit of wine diluted with half its volume of water, and then dry on blotting-paper, without heat, till the powder runs off a dry watch-glass like dry sand. Preserve in a well-closed vessel.

The equivalent of the salt (196·04) is almost exactly 7 times that of iron (28). The solution of the salt in water acidified with sulphuric acid must not become red on the addition of sulphocyanide of potassium.

5. Pure Iodine.

Preparation.—Triturate commercial iodine with $\frac{1}{6}$ of its weight of iodide of potassium, dry the mass in a large watch-glass with ground rim, warm this gently on a sand-bath, or on an iron plate, and as soon as violet fumes begin to escape, cover it with another watch-glass of the same size. Continue the application of heat until all the iodine is sublimed, and keep in a well-closed glass bottle. The chlorine or bromine, which is often found in commercial iodine, combines, in this process, with potassium, and remains in the lower watch-glass, with the excess of iodide of potassium. To carry out this operation on a larger scale, you may use a porcelain plate and large funnel, the rim of which is pasted down to the plate with strips of paper.

Tests.—Iodine thus purified must leave no fixed residue when heated on a watch-glass.

Uses.—Pure iodine is used for the preparation of the solution of iodine in iodide of potassium, employed in many volumetric processes.

6. Iodide of Potassium.

For the preparation of iodide of potassium intended for analytical purposes I recommend **Baup's** method, improved by **Frederking**, because the product obtained by this process is free from iodic acid. But it will not be worth while to make one's own iodide of potassium.

Tests.—Put a sample of the salt in dilute sulphuric acid. If the iodide is pure, it will dissolve without coloring the fluid; but if it contain iodate of potassa, the fluid will acquire a brown tint, from the presence of free iodine ($KI + HO + SO_3 = KO,SO_3 + HI$ and $IO_5 + 5\ HI = 5\ HO + 6\ I$, which remain in solution in the hydriodic acid). Mix the solution of another sample with nitrate of silver, as long as a precipitate continues to form; add solution of ammonia in excess, shake the mixture, filter, and supersaturate the filtrate with nitric acid. The formation of a white, curdy precipitate indicates the presence of chloride of potassium. Presence of sulphate of potassa is detected by means of chloride of barium, with addition of hydrochloric acid.

Uses.—Iodide of potassium is used as a solvent for iodine, in the preparation of standard solutions of iodine; it is employed also to absorb free chlorine. In the latter case every equivalent of chlorine liberates an equivalent of iodine, which is retained in solution by the agency of the excess of iodide of potassium. The iodide of potassium intended for these uses must be free from iodate and carbonate of potassa; the presence of trifling traces of chloride of potassium or sulphate of potassa is of no consequence. If a solution of iodide of potassium of an exactly known strength is required, the salt must be powdered and dried at 180° till it ceases to lose weight, before being weighed out to make the solution. If the temperature during drying much exceeds 200° the formation of iodate is to be apprehended (Pettersson[*]).

7. Sulphurous Acid.

Preparation.—Conduct the sulphurous acid gas disengaged from copper turnings and sulphuric acid, and washed (see "Qual. Anal.") into water to saturation, and keep the solution in several well-corked bottles.

This concentrated solution serves to prepare the highly dilute solution of sulphurous acid used in Bunsen's method of determining iodine.

8. Arsenious Acid.

The commercial arsenious acid in large pieces, externally opaque, but often still vitreous within, is generally quite pure. The purity of the article is tested by moderately heating it in a glass tube, open at both ends, through which a feeble current of air is transmitted. Pure arsenious acid must completely volatilize in this process; no residue must be left in the tube upon the expulsion of the sublimate from it. If a non-volatile residue is left which, when heated in a current of hydrogen gas, turns black, the arsenious acid contains teroxide of antimony, and is unfit for use in analytical processes. Dissolve about 10 grm. of the arsenious acid to be tested in soda, and add one or two drops acetate of lead. If a brownish color is produced, the arsenious acid contains sulphide of arsenic and cannot be used.

Arsenious acid is employed, in form of arsenite of soda, to determine hypochlorous acid, free chlorine, iodine, &c.

9. Chloride of Sodium.

Perfectly pure rock-salt is best suited for analytical purposes. It must dissolve in water to a clear fluid, which must not be rendered turbid by oxalate of ammonia, phosphate of soda, or chloride of barium. Pure chloride of sodium may be prepared also by Margueritte's process, viz., conduct into a concentrated solution of common salt hydrochloric gas to saturation, collect the small crystals of chloride of sodium which separate on a funnel, let them thoroughly drain, wash with hydrochloric acid, and dry the chloride of sodium finally in a porcelain dish, until the hydrochloric acid adhering to it has completely evaporated. The mother-liquor, which contains the small quantities of sulphate of lime, chloride of magnesium, &c., originally present in the salt, is at the next preparation of hydrochloric acid added to the ingredients in the retort, instead of a corresponding portion of water.

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[*] Zeitschr. f. anal. Chem. 9, 362.

Uses.—Chloride of sodium serves as a volumetric precipitating agent in the determination of silver, and also to standardize solutions of silver intended for the estimation of chlorine. We usually fuse it before weighing. The operation must be conducted with caution and must not be continued longer than necessary; for if the gas-flame acts on the salt, hydrochloric acid escapes, while carbonate of soda is formed.

10. Metallic Silver.

The silver obtained by the proper reduction of the pure chloride of the metal alone can be called chemically pure. The silver precipitated by copper, is never absolutely pure, but contains generally about $\frac{1}{1000}$ of copper.

Chemically pure silver is only used in small quantity for standardizing the chloride of sodium solution employed for the determination of silver. The solution of silver required for the estimation of chlorine need not be made with absolutely pure silver, as it is best standardized afterwards with chloride of sodium.

D. REAGENTS USED IN ORGANIC ANALYSIS.

§ 66.

1. Oxide of Copper.

Preparation.—Stir pure copper scales (which should be first ignited in a muffle) with pure nitric acid in a porcelain dish to a thick paste; after the effervescence has ceased, heat gently on the sand-bath until the mass is perfectly dry. Transfer the green basic salt produced to a Hessian crucible, and heat to a moderate redness, until no more fumes of hyponitric acid escape; this may be known by the smell, or by introducing a small portion of the mass into a test tube, closing the latter with the finger, heating to redness, and then looking through the tube lengthways. The uniform decomposition of the salt in the crucible may be promoted by stirring the mass from time to time with a hot glass rod. When the crucible has cooled a little, reduce the mass to a tolerably fine powder, pass through a metal sieve, and keep in a well stoppered bottle for use. It is always advisable to leave a small portion of the oxide in the crucible, and to expose this again to an intense red heat. This agglutinated portion is not pounded, but simply broken into small fragments.

Tests.—Pure oxide of copper is a compact, heavy, deep-black powder, gritty to the touch. Upon exposure to a red heat in a tube of hard glass with a current of air passing through, it must give no acid fumes (hyponitric acid, sulphuric acid, hydrochloric acid, selenious acid [VIOLETTE]) nor carbonic acid (from charcoal or dust). It must contain nothing soluble in water. That portion of the oxide which has been exposed to an intense red heat should be hard, and of a greyish-black color.

Uses.—Oxide of copper serves to oxidize the carbon and hydrogen of organic substances, yielding up its oxygen wholly or in part, according to circumstances. That portion of the oxide which has been heated to the most intense redness is particularly useful in the analysis of volatile fluids.

N.B. Spent oxide of copper may be regenerated by ignition in a current of oxygen or air, or by being subjected to the process detailed under its preparation. Should it have become mixed with alkaline or alkaline earthy salts, it is first digested with very dilute cold nitric acid, and washed afterwards with water.

2. CHROMATE OF LEAD.

Preparation.—Precipitate a clear filtered solution of acetate of lead, slightly acidulated with acetic acid, with a small excess of bichromate of potassa; wash the precipitate by decantation and at last *thoroughly* on a linen strainer; dry, put into a Hessian crucible, and heat to bright redness until the mass is fairly in fusion. Pour out upon a stone slab or iron plate, break, pulverize, pass through a fine metallic sieve, and keep the tolerably fine powder for use.

Tests.—Chromate of lead is a heavy powder, of a dirty yellowish-brown color. It must evolve no carbonic acid upon ignition; the evolution of carbonic acid would indicate contamination with organic matter, dust, &c. It must contain nothing soluble in water.

Uses.—Chromate of lead serves, like oxide of copper, for the combustion of organic substances. It is converted, in the process of combustion, into sesquioxide of chromium and basic chromate of lead. It suffers the same decomposition, with evolution of oxygen, when heated by itself above its point of fusion. The property of chromate of lead to fuse at a red heat renders it preferable to oxide of copper for difficultly combustible substances.

N.B. Chromate of lead may be used a second time. For this purpose it is fused again (being first washed if necessary), and then powdered. After having been twice used it is powdered, moistened with nitric acid, dried, and fused. In this way the chromate of lead may be used over and over again indefinitely (VOHL*).

3. OXYGEN GAS.

Preparation.—Triturate 100 grm. chlorate of potassa with 5 grm. of finely powdered binoxide of manganese, and introduce the mixture into a plain retort, which must not be more than half full; expose the retort, over a charcoal fire or a gas lamp, at first to a gentle, and then to a gradually increased heat. As soon as the salt begins to fuse, shake the retort a little, that the contents may be uniformly heated. The evolution of oxygen speedily commences, and proceeds rapidly at a relatively low temperature, provided the above proportions be adhered to. As soon as the air is expelled from the retort, connect the glass tube, fixed in the neck of the retort by means of a tight-fitting perforated cork, with an india-rubber tube inserted into the lower orifice of the gasometer; the glass tube must be sufficiently wide, and there must be sufficient space left around the india-rubber to permit the free efflux of the displaced water. Continue the application of heat to the retort until the evolution of gas has ceased.

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* Annal. d. Chem. u. Pharm. 106, 127.

100 grm. chlorate of potassa give about 27 litres of oxygen.

The oxygen produced by this process is moist, and may contain traces of carbonic acid gas, and also of chlorine. These impurities must be removed, and the oxygen gas thoroughly dried, before it can be used in organic analysis. The gas is, therefore, passed from the gasometer, first through a solution of potassa of 1·27 sp. gr., then through U-tubes containing granulated soda-lime, and finally according to circumstances, through U-tubes containing chloride of calcium or pumice moistened with sulphuric acid.

Tests.—A chip of wood which has been kindled and blown out, so as to leave a spark at the extremity, must immediately burst into flame in a current of oxygen gas. The gas must not render lime-water, or solution of nitrate of silver, turbid when transmitted through these fluids.

4. Soda-lime.

Preparation.—Take solution of caustic soda, ascertain its specific gravity, weigh out a certain quantity, calculate the weight of the hydrate of soda present, add twice this latter weight of the best quicklime, allow the lime to slake, and then evaporate to dryness in an iron vessel. Heat the residue in an iron or Hessian crucible, keep for some time at a low red heat, break up the lumps while still warm in an iron mortar, passing the whole through a sieve with meshes 3 mm. wide. Sift again with a mesh 2 mm. wide. The grains which remain on the sieve, and the finer portion which passes through, are kept separately in well-closed bottles.

Tests.—Soda-lime must not effervesce too much when treated with dilute hydrochloric acid in excess; but more particularly it must not evolve ammonia when mixed with pure sugar, and heated to redness.

Uses.—Granulated soda-lime forms an excellent absorbent for carbonic acid, the powder serves for the analysis of nitrogenous organic substances.

5. Metallic Copper.

Metallic copper serves, in the analysis of nitrogenous substances, to effect the reduction of the nitric oxide that may form in the course of the process.

It is used either in the form of turnings, or in that of close spirals of wire; or of small rolls made of thin sheet copper. A length of from 7 to 10 cm. is given to the spirals or rolls and just sufficient thickness to admit of their being inserted into the combustion tube. To have it perfectly free from dust, oxide, &c., it is first heated to redness in the open air, in a crucible, until the surface is oxidized; it is then put into a glass or porcelain tube, through which an uninterrupted current of dry hydrogen is transmitted; and when all atmospheric air has been expelled from the evolution apparatus and the tube, the latter is in its whole length heated to redness. The operator should make sure that the atmospheric air has been thoroughly expelled, before he proceeds to apply heat to the tube; neglect of this precaution may lead to an explosion.

6. POTASSA.

a. Solution of Potassa.

Solution of potassa is prepared from the carbonate, with the aid of milk of lime, in the way described in the "Qualitative Analysis," for the preparation of solution of soda. The proportions are—1 part of carbonate of potassa to 12 parts of water, and ⅔ part of lime, slaked to paste with three times the quantity of warm water.

The decanted clear solution is evaporated in an iron vessel, over a strong fire, to a specific gravity of 1·27; it is then, whilst still warm, poured into a bottle, which is well closed, and allowed to stand at rest until all solid particles have subsided. The clear solution is finally drawn off from the deposit, and kept for use.

b. Hydrate of Potassa (common).

The commercial hydrate of potassa in sticks will answer the purpose. If you wish to prepare it, evaporate solution of potassa (*a*) in a silver vessel, over a strong fire, until the residuary hydrate flows like oil, and white fumes begin to rise from the surface. Pour the fused mass out on a clean iron plate, and break it up into small pieces. Keep in a well-stoppered bottle for use.

c. Hydrate of Potassa (purified with alcohol), see "Qual. Anal."

Uses.—Solution of potassa serves for the absorption, and at the same time for the estimation of carbonic acid. In many cases, a tube filled with hydrate of potassa is used, in addition to the apparatus filled with solution of potassa. Hydrate of potassa purified with alcohol, which is perfectly free from sulphate of potassa, is employed for the determination of sulphur in organic substances.

7. CHLORIDE OF CALCIUM.

a. Pure Chloride of Calcium.

Preparation.—Take the residue of the preparation of ammonia, which consists of basic chloride of calcium, and digest it with warm water; or else dissolve some carbonate of lime or lime in common hydrochloric acid and water. If necessary, digest this impure solution with some hydrate of lime, so that the fluid may be strongly alkaline, and add some sulphide of calcium, till after digestion for some time a sample filtered off is not darkened by sulphide of ammonium. Now filter, render the solution barely acid with hydrochloric acid, evaporate in a porcelain dish, filter off the separated sulphur if necessary, evaporate in a porcelain dish to dryness, and expose the residue for several hours to a tolerably strong heat (about 200°), on the sand-bath. The white porous mass obtained consists of $\mathrm{Ca\,Cl} + 2\,\mathrm{aq}$.

b. Crude fused Chloride of Calcium.

Preparation.—Digest the impure solution of chloride of calcium obtained as in *a* with a little hydrate of lime, filter, neutralize exactly with hydrochloric acid, evaporate to dryness in an iron pan, fuse in an iron or Hessian crucible, pour out, and break into pieces. Preserve it in well-stoppered bottles.

Uses.—The crude fused chloride of calcium serves to dry moist gases; the pure chloride is used in organic analysis for the absorption and estimation of the water formed from the hydrogen in the substance. The solution of the pure chloride of calcium must not show an alkaline reaction.

8. BICHROMATE OF POTASSA.

The commercial salt is purified by repeated recrystallization, until a sample dissolved in water gives a precipitate with chloride of barium completely soluble in hydrochloric acid.

Bichromate of potassa thus perfectly free from sulphuric acid is required more particularly for the oxidation of organic substances with a view to the estimation of their sulphur. Where the salt is intended for other purposes, *e.g.*, to determine the carbon of organic bodies, by heating them with chromate of potassa and sulphuric acid, one recrystallization is sufficient.

SECTION III.

FORMS AND COMBINATIONS IN WHICH SUBSTANCES ARE SEPARATED FROM EACH OTHER, OR IN WHICH THEIR WEIGHT IS DETERMINED.

§ 67.

THE quantitative analysis of a compound substance requires as the first and most indispensable condition, an accurate knowledge of the composition and properties of the new combinations, into which it is intended to convert its constituents, for the purpose of separating them from one another, and determining their several weights. Regarding the properties of the new compounds, we have to inquire more particularly, in the first place, how they behave with solvents; secondly, what is their deportment in the air; and, thirdly, what is their behavior on ignition. It may be laid down as a general rule that compounds are the better adapted for being weighed the more insoluble they are, and the less alteration they undergo upon exposure to air or to a high temperature.

The composition of bodies is expressed either in per-cents, or in stoichiometrical formulæ; by means of the latter, the constitution of the more frequently recurring compounds may be easily remembered. In this Section the composition of the substances treated of is given in three different ways, in as many columns: the first column gives the composition of the substance in symbols; the second, in equivalents ($H = 1$); the third, in per-cents. With respect to its composition, a compound is the better adapted for the quantitative determination of a body the less it contains relatively of that body; since any error or loss of substance that may occur in the course of the analytical process will exercise the less influence upon the accuracy of the results. Thus, ammonio-bichloride of platinum, for instance, is, in this respect, better adapted than chloride of ammonium, for the determination of nitrogen; since the former contains only 6·295 per cent., while the latter contains 26·24 per cent. of the element in question.

Suppose we have to analyse a nitrogenous substance;—we estimate its nitrogen in the form of bichloride of platinum and chloride of ammonium. When the process is conducted with absolute accuracy, ·300 grm. of the analysed body yields 1·000 grm. of ammonio-bichloride of platinum: 100 parts of this double chloride contain 6·295 parts of nitrogen, 1·000 contains therefore ·06295 of that element. These ·06295 have been derived from ·300 of substance; 100 parts of the analysed body, consequently, contain 20·983 of nitrogen.

We now make a second analysis, in which we convert the nitrogen of the substance into chloride of ammonium: we again conduct the process with absolute accuracy, and obtain from ·300 of the substance, ·2399 of chloride of ammonium, corresponding to ·06295 of nitrogen, or 20·983 per cent.

Now, let us assume a loss of 10 milligrammes to have occurred in each process:—this will alter the result, in the first instance, from 1·000 to ·990 of bichloride of platinum and chloride of ammonium, corresponding to ·06232 of nitrogen, or 20·77 per cent.; the loss of nitrogen will therefore be 20·983 – 20·770 = ·213.

In the second instance the result will be altered from ·2399 to ·2299 of chloride of ammonium, corresponding to ·0603 of nitrogen, or 20·1 per cent. The loss in this case will consequently amount to ·873.

We see here that the same error occasions, in the one case, a loss of ·213 per cent., with respect to the amount of nitrogen; whilst, in the other case, the loss amounts to ·873 per cent.

We will now proceed to enumerate and examine those combinations of the several bodies which are best adapted for their quantitative determination. The description given of the external form and appearance of the new compounds relates more particularly to the state in which they are obtained in our analyses. With regard to the properties of the new compounds, we shall confine ourselves to the enumeration of those which bear upon the special object we have more immediately in view.

A.—FORMS IN WHICH THE BASES ARE WEIGHED OR PRECIPITATED.

BASES OF THE FIRST GROUP.

§ 68.

1. POTASSA.

The combinations best suited for the weighing of potassa are, SULPHATE OF POTASSA, NITRATE OF POTASSA, CHLORIDE OF POTASSIUM, BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM (potassio-bichloride of platinum).

a. Sulphate of potassa crystallizes usually in small, hard, straight, four-sided prisms, or in double six-sided pyramids; in the analytical process it is obtained as a white crystalline mass. It dissolves with some difficulty in water (1 part requiring 10 parts of water of 12°), it is almost absolutely insoluble in pure alcohol, but slightly more soluble in alcohol containing sulphuric acid (Expt. No. 6). It does not affect vegetable colors: it is unalterable in the air. The crystals decrepitate strongly when heated, yielding at the same time a little water, which they hold mechanically confined. The decrepitation of crystals that have been kept long drying is less marked. At a good red heat the salt fuses without volatilizing or decomposing. At a white heat a little of the salt volatilizes and also some sulphuric acid, so that the residue possesses an alkaline reaction (AL. MITSCHERLICH,* BOUSSINGAULT†). When exposed to a red heat, in conjunction with chloride of ammonium, sulphate of potassa is partly, and, upon repeated application of the process, wholly converted, with effervescence, into chloride of potassium (H. ROSE).

COMPOSITION.

KO	47·13	54·09
SO_3	40·00	45·91
	87·13	100·00

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* Journ. f. prakt. Chem. 83, 486.

† Zeitschr. f. anal. Chem. 7, 244.

Bisulphate of potassa (KO,SO_3+HO,SO_3), which is always produced when the neutral salt is evaporated to dryness with free sulphuric acid, is readily soluble in water, and fusible even at a moderate heat. At a red heat, it loses half its sulphuric acid, together with the basic water, but not readily—the complete conversion of the acid into the neutral salt requiring the long-continued application of an intense red heat. However, when heated in an atmosphere of carbonate of ammonia—which may be readily procured by repeatedly throwing into the faint red-hot crucible containing the bisulphate, small lumps of pure carbonate of ammonia, and putting on the lid—the acid salt changes readily and quickly to the neutral sulphate. The transformation may be considered complete as soon as the salt, which was so readily fusible before, is perfectly solid at a faint red heat.

b. Nitrate of potassa crystallizes generally in long striated prisms. In analysis it is obtained as a white crystalline mass; it is readily soluble in water, nearly insoluble in absolute alcohol, and sparingly soluble in spirit of wine. It does not affect vegetable colors, and is unalterable in the air. On being exposed to a gentle heat, far below redness, it fuses unaltered and without any diminution of weight; upon the application of a stronger heat, it changes into nitrite of potassa, with evolution of oxygen: and if the heat be increased to very intense redness, it becomes converted into caustic potassa, with evolution of oxygen and nitrogen. When ignited with chloride of ammonium, or in a stream of dry hydrochloric acid, it is readily and completely converted into chloride of potassium. When repeatedly evaporated with oxalic acid in excess, it is completely converted into oxalate of potassa. When evaporated with excess of hydrochloric acid repeatedly (4 to 6 times), it is completely converted into chloride of potassium.

COMPOSITION.

KO	47·13	46·58
NO_5	54·04	53·42
	101·17	100·00

c. Chloride of potassium crystallizes usually in cubes, often lengthened to columns; rarely in octahedra. In analysis we obtain it either in the former shape, or as a crystalline mass. It is readily soluble in water, but much less so in dilute hydrochloric acid; in absolute alcohol it is nearly insoluble, and but slightly soluble in spirit of wine. It does not affect vegetable colors, and is unalterable in the air. When heated, it decrepitates, unless it has been kept long drying, with expulsion of a little water mechanically confined in it. At a moderate red heat, it fuses unaltered and without diminution of weight; when exposed to a higher temperature, it volatilizes in white fumes; this volatilization proceeds the more slowly, the more effectually the access of air is prevented (Expt. No. 7). When repeatedly evaporated with solution of oxalic acid in excess, it is converted into oxalate of potassa. When evaporated with excess of nitric acid, it is converted readily and completely into nitrate. On ignition with oxalate of ammonia, carbonate of potassa and cyanide of potassium are formed in noticeable quantities.

COMPOSITION.

K	39·13	52·46
Cl	35·46	47·54
	74·59	100·00

d. Bichloride of platinum and chloride of potassium (potassio-bichloride of platinum) presents either small reddish-yellow octahedra, or a lemon-colored powder. It is difficultly soluble in cold, more readily in hot water; nearly insoluble in absolute alcohol, and but sparingly soluble in spirit of wine—one part requiring for its solution, respectively, 12083 parts of absolute alcohol, 3775 parts of spirit of wine of 76 per cent. and 1053 parts of spirit of wine of 55 per cent. (Expt. No. 8, *a*). Presence of free hydrochloric acid sensibly increases the solubility (Expt. No. 8, *b*). In caustic potassa it dissolves completely to a yellow fluid. It is unalterable in the air, and at 100°. On exposure to an intense red heat, 2 eq. of chlorine escape, metallic platinum and chloride of potassium being left; but even after long-continued fusion, there remains always a little potassio-bichloride of platinum which resists decomposition. Complete decomposition is easily effected, by igniting the double salt in a current of hydrogen gas, or with some oxalic acid.

According to ANDREWS, the bichloride of platinum and chloride of potassium, even though dried at a temperature considerably exceeding 100°, retains still ·0055 of its weight of water.

COMPOSITION.

K	39·13	16·03	KCl	74·59	30·56
Pt	98·59	40·39	$PtCl_2$	169·51	69·44
Cl_3	106·38	43·58			
	244·10	100·00		244·10	100·00

e. Silicofluoride of potassium is obtained on mixing a solution of a potassa salt with hydrofluosilicic acid in the form of a translucent iridescent precipitate, which increases and completely separates, when an equal volume of strong spirit is added to the fluid. After being filtered off, washed with weak spirit and dried, it is a soft white powder. It is difficultly soluble in cold water, far more readily in boiling water, not at all or in merest traces soluble in a mixture of water and strong spirit in equal parts, but it is decidedly more soluble in the presence of any considerable quantity of free acid, especially hydrochloric or sulphuric acid. When potassa is added to the boiling aqueous solution of the salt the following change takes place: $KF,SiF_2+2\ (HO,KO)=3\ KF+SiO_2+2\ HO$, the solution turning from acid to neutral (principle of STOLBA's volumetric method of estimating potassa). As soon as it is ignited the salt fuses, gives off fluoride of silicon and leaves fluoride of potassium.

§ 69.

2. SODA.

Soda is usually weighed as SULPHATE OF SODA, NITRATE OF SODA, CHLORIDE OF SODIUM, or CARBONATE OF SODA. It is separated from potassa in the form of SODIO-BICHLORIDE OF PLATINUM, from other bodies occasionally in the form of silicofluoride of sodium.

a. The anhydrous neutral *sulphate of soda* is a white powder or a white very friable mass. It dissolves readily in water; but is sparingly soluble in absolute alcohol; presence of free sulphuric acid slightly increases its solubility in that menstruum; it is somewhat more readily soluble in spirit of wine (Expt. No. 9). It does not affect vegetable colors; upon exposure to moist air, it slowly absorbs water (Expt. No. 10). At a gentle heat it is unaltered, at a strong red heat it fuses without decomposition or loss of weight. At a white heat it loses weight by volatilization of sulphate of soda and also of sulphuric acid. (AL. MITSCHERLICH, BOUSSINGAULT.) When ignited with chloride of ammonium it behaves like sulphate of potassa.

COMPOSITION.

NaO	31·04	43·69
SO_3	40·00	56·31
	71·04	100·00

Bisulphate of soda ($NaO,SO_3 + HO,SO_3$), which is always produced upon the evaporation of a solution of the neutral salt with sulphuric acid in excess, fuses even at a gentle heat; it may be readily converted into the neutral salt, in the same manner as the bisulphate of potassa (see § 68, *a*).

b. Nitrate of soda crystallizes in obtuse rhombohedra. In analysis it is generally obtained as an amorphous mass. It dissolves readily in water, but is as good as insoluble in absolute alcohol, and but barely soluble in spirit of wine. It does not affect vegetable colors, and is unalterable in the air under common circumstances; but when exposed to very moist air, it absorbs water. It fuses without decomposition at a temperature far below red heat (comp. Expt. No. 11), at a higher temperature it undergoes the same decomposition as nitrate of potassa (§ 68, *b*). When ignited with chloride of ammonium or in hydrochloric acid gas, and when evaporated with solution of oxalic acid, or aqueous hydrochloric acid, it comports itself like the corresponding potassa salt. The change with aqueous hydrochloric acid is effected more easily, that is, by fewer evaporations, than in the case of nitrate of potash (v. BAUMHAUER*).

COMPOSITION.

NaO	31·04	36·48
NO_5	54·04	63·52
	85·08	100·00

c. Chloride of sodium crystallizes in cubes, octahedra, and hollow four-sided pyramids. In analysis it is frequently obtained as an amorphous mass. It dissolves readily in water, but is much less soluble in hydrochloric acid; it is nearly insoluble in absolute alcohol, and but sparingly soluble in spirit of wine; 100 parts of spirit of wine of 75 per cent. dissolve, at a temperature of 15°, ·7 part (WAGNER).

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* Journ. f. prakt. Chem. 78, 218.

It is neutral to vegetable colors. Exposed to a somewhat moist atmosphere, it slowly absorbs water (Expt. No. 12). Crystals of this salt that have not been kept drying a considerable time decrepitate when heated, yielding a little water, which they hold mechanically confined. The salt fuses at a red heat without decomposition; at a white heat, and in open vessels even at a bright red heat, it volatilizes in white fumes (Expt. No. 13). If a carburetted hydrogen flame acts on fusing chloride of sodium, hydrochloric acid escapes, and some carbonate of soda is formed. On evaporation with oxalic or nitric acid as well as by ignition with oxalate of ammonia, it behaves like the corresponding potassa salt.

COMPOSITION.

Na	23·04	39·38
Cl	35·46	60·62
	58·50	100·00

d. Anhydrous *carbonate of soda* is a white powder or a white very friable mass. It dissolves readily in water, but much less so in solution of ammonia (MARGUERITTE); it is insoluble in alcohol. Its reaction is strongly alkaline. Exposed to the air, it absorbs water slowly. On moderate ignition to incipient fusion it scarcely loses weight; on long fusion, however, it volatilizes to a considerable extent (Comp. Expt. 14).

COMPOSITION.

NaO	31·04	58·52
CO_2	22·00	41·48
	53·04	100·00

e. Sodio-bichloride of platinum crystallizes with 6 eq. water ($NaCl, PtCl_2 + 6$ aq.), in light yellow, transparent, prismatic crystals which dissolve readily both in water and in spirit of wine.

f. Silicofluoride of sodium is similar in properties to the corresponding potassium salt. It has an analogous composition, and is decomposed in the same way by alkalies. It is, however, considerably more soluble in water and in diluted spirit.

§ 70.

3. AMMONIA.

Ammonia is most appropriately weighed as CHLORIDE OF AMMONIUM, or as BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM (ammonio-bichloride of platinum), or as PLATINUM.

Under certain circumstances, ammonia may also be estimated from the volume of the NITROGEN GAS eliminated from it; and it is frequently estimated by alkalimetry.

a. Chloride of ammonium crystallizes in cubes and octahedra, but more frequently in feathery crystals. In analysis we obtain it uniformly as a white mass. It dissolves readily in water, but is difficultly soluble in spirit of wine. It does not alter vegetable colors, and remains unaltered in the air. Solution of chloride of ammonium, when evaporated on the water-bath, loses a small quantity of ammonia, and becomes slightly acid. The diminution of weight occasioned by this loss of ammonia is very trifling (Expt. No. 15). At 100° chloride of ammonium loses nothing, or very little of its weight (comp. same Expt.). At a higher temperature it volatilizes readily, and without undergoing decomposition.

COMPOSITION.

NH_4 . .	18·04	33·72	NH_3. .	17·04	31·85
Cl . . .	35·46	66·28	HCl . .	36·46	68·15
	53·50	100·00		53·50	100·00

100 parts of chloride of ammonium correspond to 48·67 parts of oxide of ammonium.

b. Bichloride of platinum and chloride of ammonium occurs either as a heavy, lemon-colored powder, or in small, hard octahedral crystals of a bright yellow color. It is difficultly soluble in cold, but more readily in hot water. It is very sparingly soluble in absolute alcohol, but more readily in spirit of wine—1 part requiring of absolute alcohol, 26535 parts; of spirit of wine of 76 per cent., 1406 parts; of spirit of wine of 55 per cent., 665 parts. The presence of free acid sensibly increases its solubility (Expt. No. 16). It remains unaltered in the air, and at 100°. It loses a little water between 100 and 125°. Upon ignition chlorine and chloride of ammonium escape, leaving the metallic platinum as a porous mass (spongy platinum). However, if due care be not taken, in this process, to apply the heat gradually, the escaping fumes will carry off particles of platinum, which will coat the lid of the crucible. For properties of metallic platinum, see § 89, *a*.

COMPOSITION.

NH_4 . .	18·04	8·09	NH_4Cl . .	53·50	23·99
Pt . .	98·59	44·21	$PtCl_2$ . .	169·51	76·01
Cl_3 . .	106·38	47·70		223·01	100·00
	223·01	100·00			

NH_3 . .	17·04	7·64	N . . .	14·04	6·295
HCl . .	36·46	16·35	H_4 . . .	4·00	1·794
$PtCl_2$ . .	169·51	76·01	Pt . . .	98·59	44·209
	223·01	100·00	Cl_3 . . .	106·38	47·702
				223·01	100·00

100 parts of ammonio-bichloride of platinum correspond to 11·677 parts of oxide of ammonium.

c. Nitrogen gas is colorless, tasteless, and inodorous; it mixes with air, without producing the slightest coloration; it does not affect vegetable colors. Its specific gravity is ·97137 (REGNAULT). One litre weighs at 0°, and ·76 metre bar., 1·25617 grm. It is difficultly soluble in water, 1 volume of water absorbing, at 0°, and ·76 pressure, ·02035 vol.; at 10°, ·01607 vol.; at 15°, ·01478 vol. of nitrogen gas (BUNSEN).

BASES OF THE SECOND GROUP.

§ 71.

1. BARYTA.

Baryta is weighed as SULPHATE OF BARYTA, CARBONATE OF BARYTA, and SILICOFLUORIDE OF BARIUM.

a. Artificially prepared *sulphate of baryta* presents the appearance of a fine white powder. When recently precipitated, it is difficult to obtain a clear filtrate, especially if the precipitation was effected in the cold, and the solution contains neither hydrochloric acid nor chloride of ammonium. It is as good as insoluble in cold and in hot water. (1 part of the salt requires more than 400,000 parts of water for solution). It has a great tendency, upon precipitation, to carry down with it other substances contained in the solution from which it separates, more particularly nitrate of baryta, alkaline nitrates and chlorates, sesquioxide of iron, &c. Several of the impurities, such, for instance, as alkaline chlorates, may be removed by igniting the sulphate of baryta, moistening with hydrochloric acid, evaporating the latter off and exhausting the residue with water; other impurities again, such as alkaline nitrates, cannot be removed by this treatment.* Even the precipitate obtained from a solution of chloride of barium by means of sulphuric acid in excess contains traces of chloride of barium, which it is impossible to remove, even by washing with boiling water, but which are dissolved by nitric acid (SIEGLE). Cold dilute acids dissolve trifling, yet appreciable traces of sulphate of baryta; for instance, 1000 parts of nitric acid of 1·032 sp. gr. dissolve ·062 parts (CALVERT), 1000 parts of hydrochloric acid containing 3 per cent. dissolve ·06 parts.* Cold concentrated acids dissolve considerably more; thus, 1000 parts of nitric acid of 1·167 sp. gr. dissolve 2 parts (CALVERT). Boiling hydrochloric acid also dissolves appreciable traces; thus 230 c.c. hydrochloric acid of 1·02 sp. gr. were found, after a quarter of an hour's boiling with ·679 grm. sulphate of baryta, to have dissolved of it ·048 grm. Acetic acid dissolves less sulphate of baryta than the other acids; thus, 80 c.c. acetic acid of 1·02 sp. gr. were found, after a quarter of an hour's boiling with ·4 grm. to have dissolved only ·002 grm. (SIEGLE). Free chlorine considerably increases its solubility (O. L. ERDMANN). Several salts more particularly interfere with the precipitation of baryta by sulphuric acid. I observed this some time ago with chloride of magnesium, but nitrate of ammonia (MITTENTZWEY), alkaline nitrates generally,* and more particularly alkaline citrates (SPILLER), possess this property in a high degree. In the last case the precipitate appears on the addition of hydrochloric acid. If a fluid contains metaphosphoric acid, baryta cannot be completely precipitated out of it by means of sulphuric acid; the resulting precipitate too contains phosphoric acid (SCHEERER, RUBE). Sulphate of baryta dissolves in tolerable quantity in concentrated sulphuric acid, but separates again on dilution. It is as good as insoluble in a boiling solution of sulphate of ammonia (1 in 4). Sulphate of baryta remains quite unaltered in the air, at 100°, and even at a red heat. At a strong white heat it loses sulphuric acid (Boussingault).* On ignition with charcoal, or under the influence of reducing gases, it is converted comparatively easily, but as a rule only partially, into sulphide of barium. On ignition with chloride of ammonium, sulphate of baryta undergoes partial decomposition. It is not affected, or affected but very slightly, by cold solutions of alkaline bicarbonates or of carbonate of ammonia; solutions of the monocarbonates of the fixed alkalies when cold have only a slight decomposing action upon it; but when boiling, and upon repeated application, they effect at last the complete decomposition of the salt (H. Rose). By fusion with alkaline carbonates, sulphate of baryta is readily decomposed.

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* Compare my paper on the Estimation of Sulphuric Acid, Zeitschr. f. anal. Chem. 9, 62.

COMPOSITION.

BaO	76·5	65·67
SO_3	40·0	34·33
	116·5	100·00

b. Artificially prepared *carbonate of baryta* presents the appearance of a white powder. It dissolves in 14137 parts of cold, and in 15421 parts of boiling water (Expt. No. 17). It dissolves far more readily in solutions of chloride of ammonium or nitrate of ammonia; from these solutions it is, however, precipitated again, though not completely, by caustic ammonia. In water containing free carbonic acid, carbonate of baryta dissolves to bicarbonate. In water containing ammonia and carbonate of ammonia, it is nearly insoluble, one part requiring about 141000 parts (Expt. No. 18). Its solution in water has a very faint alkaline reaction. Alkaline citrates and metaphosphates impede the precipitation of baryta by carbonate of ammonia. It is unalterable in the air, and at a red heat. When exposed to the strongest heat of a blast-furnace, it slowly yields up the whole of its carbonic acid; this expulsion of the carbonic acid is promoted by the simultaneous action of aqueous vapor. Upon heating it to redness with charcoal, caustic baryta is formed, with evolution of carbonic oxide gas.

COMPOSITION.

BaO	76·5	77·67
CO_2	22·0	22·33
	98·5	100·00

c. Silicofluoride of barium forms small, hard, and colorless crystals, or (more generally) a crystalline powder. It dissolves in 3800 parts of cold water; in hot water it is more readily soluble (Expt. No. 19). The presence of free hydrochloric acid increases its solubility considerably (Expt. No. 20). Chloride of ammonium acts also in the same way (1 part silicofluoride of barium dissolves in 428 parts of saturated, and 589 parts of dilute solution of chloride of ammonium. J. W. Mallet). In spirit of wine it is almost insoluble. It is unalterable in the air, and at 100°; when ignited, it is decomposed into fluoride of silicon, which escapes, and fluoride of barium, which remains.

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* Zeitschr. f. anal. Chem. 7, 244.

COMPOSITION.

Ba F . .	87·5	62·72	Ba	68·5	49·10
$Si F_3$ . .	52·0	37·28	Si	14·0	10·04
			F_3	57·0	40·86
	139·5	100·00		139·5	100·00

§ 72.

2. STRONTIA.

Strontia is weighed either as SULPHATE OF STRONTIA, or as CARBONATE OF STRONTIA.

a. Sulphate of strontia, artificially prepared, is a white powder, sometimes dense and crystalline, sometimes loose and bulky. It dissolves in 6895 parts of cold, and 9638 parts of boiling water (Expt. No. 21). In water containing sulphuric acid, it is still more difficultly soluble, requiring from 11000 to 12000 parts (Expt. No. 22). Of cold hydrochloric acid of 8·5 per cent., it requires 474 parts; of cold nitric acid of 4·8 per cent., 432 parts; of cold acetic acid of 15·6 per cent. of $\bar{A}$,HO, as much as 7843 parts (Expt. No. 23). It dissolves in solutions of chloride of potassium and chloride of magnesium in quantity which increases with the concentration, also in solutions of chloride of sodium and chloride of calcium in greatest quantity when the solutions are of medium concentration (A. VIRCK*); it is precipitated from these solutions by sulphuric acid. Metaphosphoric acid (SCHEERER, RUBE), and also alkaline citrates. but not free citric acid (SPILLER), impede the precipitation of strontia by sulphuric acid. It is as good as insoluble in absolute alcohol, in spirit of wine, and in a boiling solution of sulphate of ammonia (1 in 4). It does not alter vegetable colors; and remains unaltered in the air, and at a red heat. When exposed to a most intense red heat, it fuses with loss of a small quantity of sulphuric acid (M. DARMSTADT†); all the sulphuric acid will escape on very strong ignition continued for a length of time (BOUSSINGAULT‡). When ignited with charcoal, or under the influence of reducing gases, it is converted into sulphide of strontium. The solutions of carbonates and bicarbonates of potassa, soda, and ammonia decompose sulphate of strontia completely at the common temperature, even when considerable quantities of alkaline sulphates are present (H. ROSE). Boiling promotes the decomposition.

COMPOSITION.

SrO	51·75	56·40
SO_3	40·00	43·60
	91·75	100·00

b. Carbonate of strontia, artificially prepared, is a white, soft, loose powder. It dissolves, at the common temperature, in 18045 parts of water (Expt. No. 24): presence of ammonia diminishes its solubility (Expt. No. 25). It dissolves pretty readily in solutions of chloride of ammonium and nitrate of ammonia, but is precipitated again from these solutions by ammonia and carbonate of ammonia, and more completely than carbonate of baryta under similar circumstances. Water impregnated with carbonic acid dissolves it as bicarbonate. Its reaction is very feebly alkaline. Alkaline citrates and metaphosphates impede the precipitation of strontia by alkaline carbonates. Ignited with access of air it is infusible, but when exposed to a most intense heat, it fuses and gradually loses its carbonic acid. On ignition with charcoal, caustic strontia is formed, with evolution of carbonic oxide gas.

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* Zeitschr. f. anal. Chem. 1, 473. † Ib. 6, 376. ‡ Ib. 7, 244.

COMPOSITION.

SrO	51·75	70·17
CO_2	22·00	29·83
	73·75	100·00

§ 73.

3. LIME.

Lime is weighed either as SULPHATE OF LIME, CARBONATE OF LIME, or CAUSTIC LIME; to convert it into the latter forms, it is first usually precipitated as oxalate of lime.

a. Artificially prepared anhydrous *sulphate of lime* is a loose, white powder. It dissolves, at the common temperature, in 430 parts, at 100°, in 460 parts of water (POGGIALE). Presence of hydrochloric acid, nitric acid, chloride of ammonium, sulphate of soda, or chloride of sodium, increases its solubility. It dissolves with comparative ease, especially on gently warming, in aqueous solution of hyposulphite of soda (DIEHL), and also in a boiling solution of sulphate of ammonia (1 in 4). The aqueous solution of sulphate of lime does not alter vegetable colors. In alcohol and in spirit of wine of 90 per cent. it is almost absolutely insoluble. Exposed to the air, it slowly absorbs water. It remains unaltered at a dull red heat. Heated to intense bright redness, it fuses, losing weight considerably from loss of sulphuric acid (AL. MITSCHERLICH*). On long ignition at a white heat all the sulphuric acid escapes (BOUSSINGAULT†). On ignition with charcoal or under the influence of reducing gases it is converted into sulphide of calcium. Solutions of alkaline carbonates and bicarbonates decompose sulphate of lime more readily still than sulphate of strontia.

COMPOSITION.

CaO	28	41·18
SO_3	40	58·82
	68	100·00

b. Carbonate of lime artificially produced by the precipitation of a lime salt with carbonate of ammonia is at first loose and amorphous, but after some time becomes a white, fine, crystalline powder, which under the microscope has sometimes the form of calcite, sometimes that of aragonite. It is very slightly soluble in water. By protracted boiling 1 litre of water dissolves ·034 grm. according to A. W. HOFMANN, or ·036 grm. according to C. WELTZIEN; so one part requires 28500 parts of water for solution. The solution has a barely perceptible alkaline reaction. In water containing ammonia and carbonate of ammonia the crystallized salt dissolves much more sparingly (Expt. No. 26), one part requiring about 65000 parts; this solution is not precipitated by oxalate of ammonia. Amorphous carbonate of lime is also much more insoluble in water containing ammonia than in pure water (DIVERS*). Presence of chloride of ammonium and of nitrate of ammonia increases the solubility of carbonate of lime; but the salt is precipitated again from these solutions by ammonia and carbonate of ammonia, and more completely than carbonate of baryta under similar circumstances. Neutral salts of potassa and soda, and also neutral salts of lime and magnesia (HUNT), likewise increase its solubility. The precipitation of lime by alkaline carbonate is completely prevented or considerably interfered with by the presence of alkaline citrates (SPILLER) or metaphosphates (RUBE). Water impregnated with carbonic acid dissolves carbonate of lime as bicarbonate. Carbonate of lime remains unaltered in the air, at 100°, and even at a low red heat; but upon the application of a stronger heat, more particularly with free access of air, it gradually loses its carbonic acid. By means of a gas blowpipe-lamp, carbonate of lime (about ·5 grm.), in an open platinum crucible, is without difficulty reduced to the caustic state; attempts to effect complete reduction over a spirit lamp with double-draught have, however, failed (Expt. No. 27). It is decomposed far more readily when ignited with charcoal, giving off its carbonic acid in the form of carbonic oxide.

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* Journ. f. prakt. Chem. 83, 485.

† Zeitschr. f. anal. Chem. 7, 244.

COMPOSITION.

CaO	28	56·00
CO_2	22	44·00
	50	100·00

c. *Oxalate of lime*, precipitated from hot or concentrated solutions, is a fine white powder consisting of infinitely minute indistinct crystals, and almost absolutely insoluble in water. If the oxalic acid is held to be bibasic, the salt has the formula, $2CaO,C_4O_6 + 2$ aq. When precipitated from cold, extremely dilute solutions, the salt presents a more distinctly crystalline appearance, and consists of a mixture of $2CaO,C_4O_6 + 2$ aq. and $2CaO,C_4O_6 + 6$ aq. (SOUCHAY and LENSSEN). Presence of free oxalic acid and acetic acid slightly increases the solubility of oxalate of lime. The stronger acids (hydrochloric acid, nitric acid) dissolve it readily; from these solutions it is precipitated again unaltered, by alkalies, and also (provided the excess of acid be not too great) by alkaline oxalates or acetates added in excess. Oxalate of lime does not dissolve in solutions of chloride of potassium, chloride of sodium, chloride of ammonium, chloride of barium, chloride of calcium, and chloride of strontium, even though these solutions be hot and concentrated; but, on the other hand, it dissolves readily and in appreciable quantities, in hot solutions of the salts belonging to the magnesia group.

* Journ. Chem. Soc. 1870, 362.

From these solutions it is reprecipitated by an excess of alkaline oxalate (Souchay and Lenssen). Alkaline citrates (Spiller) and metaphosphates (Rube) impede the precipitation of lime by alkaline oxalates. When treated with solutions of many of the heavy metals, *e.g.*, with solution of chloride of copper, nitrate of silver, &c., oxalate of lime suffers decomposition, a soluble salt of lime being formed, and an oxalate of the heavy metallic oxide, which separates immediately, or after some time (Reynoso). Oxalate of lime is unalterable in the air, and at 100°. Dried at the latter temperature, it has invariably the following composition (Expt. No. 28, also Souchay and Lenssen[*]).

2CaO	56	38·36
C_4O_6	72	49·32
2 aq.	18	12·32
	146	100·00

At 205° oxalate of lime loses its water, without undergoing decomposition; at a somewhat higher temperature, still scarcely reaching dull redness, the anhydrous salt is decomposed, without actual separation of carbon, into carbonic oxide and carbonate of lime. The powder, which was previously of snowy whiteness, transiently assumes a gray color in the course of this process, even though the oxalate be perfectly pure. Upon continued application of heat this gray color disappears again. If the oxalate of lime is heated in small coherent fragments, such as are obtained upon drying the precipitated salt on a filter, the commencement and progress of the decomposition can be readily traced by this transient appearance of gray. If the process of heating be conducted properly, the residue will not contain a trace of caustic lime. Hydrated oxalate of lime exposed suddenly to a dull red heat, is decomposed with considerable separation of carbon. By ignition over the gas blowpipe oxalate of lime is converted into caustic lime.

d. Lime obtained by continued strong ignition of the oxalate or carbonate appears as a white, infusible powder, unalterable by ignition. By standing in the air it attracts water and carbonic acid, but not rapidly enough to interfere with accurate weighing (Expt. No. 29). By treatment with a little water the hydrate is formed with evolution of much heat; on igniting again the water of hydration is readily and completely removed. Pure lime dissolves in dilute hydrochloric acid with evolution of heat, but without effervescence.

§ 74.

4. Magnesia.

Magnesia is weighed as SULPHATE OF MAGNESIA, PYROPHOSPHATE OF MAGNESIA, or PURE MAGNESIA. To convert it into the pyrophosphate, it is precipitated as BASIC PHOSPHATE OF AMMONIA AND MAGNESIA.

a. Anhydrous *sulphate of magnesia* presents the appearance of a white, opaque mass. It dissolves readily in water. It is nearly altogether insoluble in absolute alcohol, but it is somewhat soluble in spirit of wine. It does not alter vegetable colors. Exposed to the air it absorbs water rapidly. At a moderate red heat, it remains unaltered; but when heated to intense redness, it undergoes partial decomposition, losing part of its acid, after which it is no longer perfectly soluble in water. By means of a gas blowpipe it is tolerably easy to expel the whole of the sulphuric acid from small quantities of sulphate of magnesia (Expt. No. 30). Ignited with chloride of ammonium, sulphate of magnesia is not decomposed.

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[*] Annal. d. Chem. und Pharm. 100, 322.

COMPOSITION.

MgO	20	33·33
SO_3	40	66·67
	60	100·00

b. Basic phosphate of magnesia and ammonia is a white crystalline powder. It dissolves, at the common temperature, in 15293 parts of cold water (Expt. No. 31). In water containing ammonia, it is much more insoluble. 1000 grm. of a mixture of 3 parts water and 1 part ammonia solution, dissolved only a quantity corresponding to ·004 grm. pyrophosphate (Kissel*); the salt was considerably more soluble when chloride of ammonium was also present; thus in one of Kissel's experiments a quantity corresponding to ·011 grm. pyrophosphate was dissolved by 1000 grm. fluid containing 18 grm. chloride of ammonium. Presence of excess of sulphate of magnesia diminishes the solubility in dilute ammonia, even in the presence of chloride of ammonium, to such an extent that the quantity dissolved by 1000 grm. fluid cannot be estimated (Kissel); the precipitate, under these circumstances, is liable, especially in the absence of much chloride of ammonium, and when the excess of sulphate of magnesia is large, to contain some hydrate or basic sulphate of magnesia (Kubel,† Kissel). Phosphate of soda also diminishes (to about the same extent as sulphate of magnesia) the solubility of the salt in water containing chloride of ammonium and ammonia (W. Heintz‡). It dissolves readily in acids, even in acetic acid. Its composition is expressed by the formula, $2MgO,NH_4O,PO_5 + 12\,aq$. 10 eq. of water escape at 100°, the remaining two together with the ammonia, at a red heat, leaving $2MgO,PO_5$. On the application of a stronger heat the mass passes through a state of incandescence, if the salt were pure; the weight of the residue is not affected. The incandescence may not take place at all in the presence of small quantities of lime salts, of other magnesia salts, or of silicic acid. It is occasioned not by the passage of the phosphoric acid into pyrophosphoric acid, but by the passage from the crystalline to the amorphous condition (O. Popp§). If phosphate of magnesia and ammonia is dissolved in dilute hydrochloric or nitric acid and ammonia be then added to the solution, the salt is reprecipitated completely, or more correctly, only so much remains in solution as corresponds to its ordinary solubility in water containing ammonia and ammoniacal salt.

c. Pyrophosphate of magnesia presents the appearance of a white mass, often slightly inclining to gray. It is barely soluble in water, but readily so in hydrochloric acid, and in nitric acid. It remains unaltered in the air, and at a red heat; at a very intense heat it fuses unaltered. Exposed at a white heat to the action of hydrogen, $3MgO,PO_5$ is formed, while PH_3, P and PO_3 escape. $3\,(2MgO,PO_5) = 2\,(3MgO,PO_5) + PO_5$ (STRUVE*). It leaves the color of moist turmeric-, and of reddened litmus-paper unchanged. If we dissolve it in hydrochloric or nitric acid, add water to the solution, boil for some time, and then precipitate with ammonia in excess, we obtain a precipitate of phosphate of magnesia and ammonia which, after ignition, affords less $2MgO,PO_5$, than was originally employed. WEBER† gives the loss as from 1·3 to 2·3 per cent. My own experiments (No. 32) confirm this statement, and point out the circumstances under which the loss is the least considerable. By long-continued fusion with mixed carbonates of potassa and soda, pyrophosphate of magnesia is completely decomposed, the phosphoric acid being reconverted into the tribasic state. If, therefore, we treat the fused mass with hydrochloric acid, and then add water and ammonia, we re-obtain on igniting the precipitate the whole quantity of the salt used. If the solution of pyrophosphate of magnesia in nitric acid is evaporated to dryness, a white residue is left; if this is heated more strongly hyponitric acid is liberated, and the residue turns the color of cinnamon; on cooling it is yellowish-white. By heating still more strongly to incipient redness, rapid decomposition sets in, more hyponitric acid is evolved, and pure white pyrophosphate of magnesia is left. Unless the heat is applied with care the evolution of gas may be so rapid as to carry away particles of the substance (E. LUCK).

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* Zeitschr. f. anal. Chem. 8, 173.

† Ib. 8, 125.

‡ Ib. 9, 16.

§ Ib. 13, 305.

COMPOSITION.

$2MgO$	40·00	36·04
PO_5	71·00	63·96
	111·00	100·00

d. Pure magnesia is a white, light, loose powder. It dissolves in 55368 parts of cold, and in the same proportion of boiling water (Expt. No. 33). Its aqueous solution has a very slightly alkaline reaction. Magnesia dissolves in hydrochloric and in other acids, without evolution of gas. Magnesia dissolves readily and in quantity, in solutions of neutral ammonia salts, and also in solutions of chloride of potassium and chloride of sodium (Expt. No. 34) and sulphate of potassa and sulphate of soda (R. WARINGTON, Jun.) it is more soluble than in water. Exposed to the air, it slowly absorbs carbonic acid and water. Magnesia is highly infusible, remaining unaltered at a strong red heat, and fusing superficially only at the very highest temperature.

COMPOSITION.

Mg	12	60·00
O	8	40·00
	20	100·00

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* Journ. f. prakt. Chem. 79, 349.

† Pogg. Ann. 73, 146.

BASES OF THE THIRD GROUP.

§ 75.

1. ALUMINA.

Alumina is usually precipitated as HYDRATE, occasionally as BASIC ACETATE or BASIC FORMATE, and always weighed in the PURE STATE.

a. Hydrate of alumina, recently precipitated from a solution of an alumina salt by an alkali is translucent, and when dried at 100° has the formula, $Al_2O_3,3HO$. The precipitate invariably retains a minute proportion of the acid with which the alumina was previously combined, as well as of the alkali which has served as the precipitant; it is freed with difficulty from these admixtures by repeated washing. It is insoluble in pure water; but it readily dissolves in soda, potassa, and ethylamine (SONNENSCHEIN); it is sparingly soluble in ammonia, and insoluble in carbonate of ammonia; presence of ammoniacal salts greatly diminishes its solubility in ammonia (Expt. No. 35). The correctness of this statement of mine in the first edition of the present work, has been amply confirmed since by MALAGUTI and DUROCHER;* and also by experiments made by my former assistant, Mr. J. FUCHS. The former chemists state also that, when a solution of alumina is precipitated with sulphide of ammonium, the fluid may be filtered off five minutes after, without a trace of alumina in it. FUCHS did not find this to be the case (Expt. No. 36). Hydrate of alumina, recently precipitated, dissolves readily in hydrochloric or nitric acid; but after filtration, or after having remained for some time in the fluid from which it has been precipitated, it does not dissolve in these acids without considerable difficulty, and long digestion. Hydrate of alumina shrinks considerably on drying, and then presents the appearance of a hard, translucent, yellowish, or of a white, earthy mass. When ignited, it loses its water, and this loss is frequently attended with slight decrepitation, and invariably with considerable diminution of bulk.

Hydrate of alumina precipitated from a solution of alumina in potassa or soda by chloride of ammonium is milk-white, denser, easier to wash, and much less soluble in ammonia than the variety above described. When dried at 100°, it has the formula $Al_2O_3,2HO$ (J. LÖWE†).

b. Alumina, prepared by heating the hydrate to a moderate degree of redness, is a loose and soft mass; but upon the application of a very intense degree of heat, it concretes into small, hard lumps. At the most intense white heat, it fuses to a clear glass. Ignited alumina is dissolved by dilute acids with very great difficulty; in fuming hydrochloric acid, it dissolves upon long-continued digestion in a warm place, slowly, but completely. It dissolves tolerably easily and quickly by first heating with a mixture of 8 parts of concentrated sulphuric acid and 3 parts of water, and then adding water (A. MITSCHERLICH‡). Ignition in a current of hydrogen gas leaves it unaltered. By fusion with bisulphate of potassa, it is rendered soluble in water. Upon igniting alumina with chloride of ammonium, chloride of aluminium escapes; but the process fails to effect complete volatilization of the alumina (H. Rose). When alumina is fused at a very high temperature, with ten times its quantity of carbonate of soda, aluminate of soda is formed, which is soluble in water (R. Richter). Placed upon moist red litmus-paper, pure alumina does not change the color to blue.

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* Ann. de Chim. et de Phys. 3 Sér. 17, 421.

† Zeitschr. f. anal. Chem. 4, 350.

‡ Journ. f. prakt. Chem. 81, 110.

COMPOSITION.

Al_2	27·50	53·40
O_3	24·00	46·60
	51·50	100·00

c. If to the solution of a salt of alumina, carbonate of soda or carbonate of ammonia be added, till the resulting precipitate only just redissolves on stirring, and then acetate of soda or acetate of ammonia poured in in abundance and the mixture boiled some time, the alumina is precipitated almost completely as basic acetate in the form of translucent flocks, so that if the filtrate be boiled with chloride of ammonium and ammonia only unweighable traces of alumina separate. If the quantity of acetate of soda employed be too small, the precipitate appears more granular, the filtrate would then contain a larger amount of alumina. The precipitate cannot be very conveniently filtered and washed. In washing it is best to use boiling water, containing a little acetate of soda or acetate of ammonia. The precipitate is readily soluble in hydrochloric acid.

d. If, instead of the acetates mentioned in *c*, the corresponding formates be used, a flocculent voluminous precipitate of basic formate of alumina is obtained, which may be very readily washed (Fr. Schulze*).

§ 76.

2. Sesquioxide of Chromium.

Sesquioxide of chromium is usually precipitated as HYDRATE, and always weighed in the pure state.

a. Hydrated sesquioxide of chromium, recently precipitated from a green solution, is greenish-gray, gelatinous, insoluble in water: it dissolves readily, in the cold, in solutions of potassa or soda, to a dark green fluid; it dissolves also in the cold, but rather sparingly, in solution of ammonia, to a light violet red fluid. In acids it dissolves readily, with a dark green color. Presence of chloride of ammonium exercises no influence upon the solubility of the hydrate in ammonia. Boiling effects the complete separation of the sesquioxide from its solutions in potassa, or ammonia (Expt. No. 37). The dried hydrate is a greenish-blue powder; it loses its water of hydration at a gentle red heat.

b. Sesquioxide of chromium, produced by heating the hydrate to dull redness, is a dark green powder; upon the application of a higher degree of heat, it assumes a lighter tint, but suffers no diminution of weight; the transition from the darker to the lighter tint is marked by a vivid incandescence of the powder. The feebly ignited sesquioxide is difficultly soluble in hydrochloric acid, and the strongly ignited sesquioxide is altogether insoluble in that acid. It remains unaltered when ignited with chloride of ammonium, or in a current of hydrogen. By fusion with carbonate of soda and nitrate of potassa chromate of potassa is formed.

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* Chem. Centralbl. 1861, 3.

COMPOSITION.

Cr_2	52·48	68·62
O_3	24·00	31·38
	76·48	100·00

BASES OF THE FOURTH GROUP.

§ 77.

1. Oxide of Zinc.

Zinc is weighed in the form of OXIDE or SULPHIDE; it is precipitated as BASIC CARBONATE, or as SULPHIDE.

a. Basic carbonate of zinc, recently precipitated, is white, flocculent, nearly insoluble in water—(one part requiring 44000 parts, Expt. No. 38)—but readily soluble in potassa, soda, ammonia, carbonate of ammonia, and acids. The solutions in soda or potassa, if concentrated, are not altered by boiling; but if dilute, nearly all the oxide of zinc present is thrown down as a white precipitate. From the solutions in ammonia and carbonate of ammonia, especially if they are dilute, oxide of zinc likewise separates upon boiling. When a neutral solution of zinc is precipitated with carbonate of soda or carbonate of potassa, carbonic acid is evolved, since the precipitate formed is not ZnO,CO_2, but consists of a compound of hydrated oxide of zinc with carbonate of zinc in proportions varying according to the concentration of the solution, and to the mode of precipitation. Owing to the presence and action of this carbonic acid, part of the oxide of zinc remains in solution; if filtered cold, therefore, the filtrate gives a precipitate with sulphide of ammonium. But if the solution is precipitated boiling, and kept at that temperature for some time, the precipitation of the zinc is complete to the extent that the filtrate is not rendered turbid by sulphide of ammonium; still, if the filtrate, mixed with sulphide of ammonium, be allowed to stand at rest for many hours, minute and almost unweighable flakes of sulphide of zinc will separate from the fluid. The precipitate of carbonate of zinc, obtained in the manner just described, may be completely freed from all admixture of alkali by washing with hot water. If ammoniacal salts be present, the precipitation is not complete till every trace of ammonia is expelled. If the solution of a zinc salt is mixed with carbonate of potassa or soda in excess, the mixture evaporated to dryness, at a gentle heat, and the residue treated with cold water, a perceptible proportion of the zinc is obtained in solution as double carbonate of zinc and potassa or soda; but if the mixture is evaporated to dryness, at boiling heat, and the residue treated with hot water, the whole of the zinc, with the exception of an extremely minute proportion, as we have already had occasion to observe, is obtained as carbonate of zinc. The dried basic carbonate of zinc is a brilliant, white, loose powder; exposure to a red heat converts it into oxide.

b. Oxide of zinc, produced from the carbonate by ignition, is a white light powder, with a slightly yellow tint. When heated, it acquires a yellow color, which disappears again on cooling. Upon ignition with charcoal, carbonic oxide and zinc fumes escape. By igniting in a rapid current of hydrogen, metallic zinc is produced; whilst by igniting in a feeble current of hydrogen, crystallized oxide of zinc is obtained (ST. CLAIRE DEVILLE). In the latter case, too, a portion of the metal is reduced and volatilized. Oxide of zinc is insoluble in water. Placed on moist turmeric paper, it does not change the color to brown. In acids, oxide of zinc dissolves readily and without evolution of gas. Ignited with chloride of ammonium, fused chloride of zinc is produced which volatilizes with very great difficulty if the air is excluded: but readily and completely, with free access of air, and with chloride of ammonium fumes. Mixed with a sufficiency of powdered sulphur and ignited in a stream of hydrogen, the corresponding amount of sulphide is obtained (H. ROSE).

COMPOSITION.

Zn	32·53	80·26
O	8·00	19·74
	40·53	100·00

c. Sulphide of zinc, recently precipitated, is a white, loose hydrate. The following facts should here be mentioned with regard to its precipitation.* Colorless sulphide of ammonium precipitates dilute solutions of zinc, but only slowly; yellow sulphide of ammonium does not precipitate dilute solutions of zinc (1 : 5000) at all. Chloride of ammonium favors the precipitation considerably. Free ammonia acts so as to keep the precipitate somewhat longer in suspension, otherwise it exerts no injurious influence. If the conditions which I shall lay down are strictly observed oxide of zinc may be precipitated by sulphide of ammonium from a solution containing only $\frac{1}{800000}$. Hydrated sulphide of zinc on account of its slimy nature easily stops up the pores of the filter, and cannot therefore be washed without difficulty on a filter. The washing is best performed by using water containing sulphide of ammonium, and continually diminished quantities of chloride of ammonium (at last none) (see Expt. No. 39). The hydrate is insoluble in water, in caustic alkalies, alkaline carbonates, and the monosulphides of the alkali metals. It dissolves readily and completely in hydrochloric and in nitric, but only very sparingly in acetic acid. When dried, the precipitated sulphide of zinc is a white powder; when air-dried its composition is $3ZnS,2HO$; dried at 100°, $2ZnS,HO$; at 150°, $4ZnS,HO$ (A. SOUCHAY†). On ignition it loses the whole of its water. During the latter process some sulphuretted hydrogen escapes, and the residue contains some oxide. By roasting in the air, and intense ignition, small quantities of sulphide of zinc may be readily converted into the oxide. On igniting the dried sulphide of zinc, mixed with powdered sulphur, in a stream of hydrogen, the pure anhydrous sulphide is obtained (H. ROSE). The latter suffers no loss of weight worth mentioning by ignition for five minutes over the gas blowpipe; but if such ignition is very protracted the loss of weight becomes considerable (AL. CLASSEN‡).

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* Journ. f. prakt. Chem. 82, 263.

† Zeitschr. f. anal. Chem. 7, 78.

‡ *Ib.* 4, 421.

COMPOSITION.

Zn	32·53	67·03
S	16·00	32·97
	48·53	100·00

§ 78.

2. Protoxide of Manganese.

Manganese is weighed either as PROTOSESQUIOXIDE, as SULPHIDE, as PROTOSULPHATE, or as PYROPHOSPHATE. With the view of converting it into these forms, it is precipitated as PROTOCARBONATE, HYDRATED PROTOXIDE, BINOXIDE, or PHOSPHATE OF MANGANESE AND AMMONIA.

a. Carbonate of manganese, recently precipitated, is white, flocculent, nearly insoluble in pure water, but somewhat more soluble in water impregnated with carbonic acid. Presence of carbonate of soda or potassa does not increase its solubility. Recently precipitated carbonate of manganese dissolves pretty readily in chloride of ammonium: it is owing to this property that a solution of manganese cannot be completely precipitated by carbonate of potassa or soda, in presence of chloride of ammonium (or any other ammoniacal salt), until the latter is completely decomposed. If the precipitate, while still moist, is exposed to the air, or washed with water impregnated with air, especially if it is in contact with carbonated alkali, it slowly assumes a dirty brownish-white color, part of it becoming converted into hydrated protosesquioxide of manganese. Even long-continued washing will not remove the last traces of alkali salt from the precipitate. The wash-water often comes through turbid. If the filtrate and wash-water are evaporated to dryness and the residue is treated with boiling water the small traces of carbonate of manganese which were partly dissolved and partly suspended will remain behind in the form of hydrated protosesquioxide. Dried by pressure the precipitate is white, and consists of $MnO,CO_2 + HO$; dried in a vacuum it consists of $2(MnO,CO_2) + HO$ (E. Prior*); when dried with free access of air, the powder is of a dirty-white color. When strongly heated with access of air, this powder first turns black, and changes subsequently to brown protosesquioxide of manganese. However, this conversion takes some time, and must never be held to be completed until two weighings, between which the precipitate has been ignited again with free access of air, give perfectly corresponding results. On igniting the carbonate of manganese, mixed with powdered sulphur, in a stream of hydrogen, sulphide of manganese is obtained (H. Rose).

b. Hydrated protoxide of manganese recently thrown down forms a white, flocculent precipitate, barely soluble in water and alkalies, but soluble in chloride of ammonium; it immediately absorbs oxygen from the air, and turns brown, owing to the formation of the hydrated protosesquioxide. On drying it in the air, a brown powder (hydrated protosesquioxide of manganese) is obtained which, when heated to intense redness, with free access of air, is converted into protosesquioxide, and on ignition with sulphur, in a stream of hydrogen, is converted into sulphide.

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* Zeitschr. f. anal Chem. 8, 428.

c. Protosesquioxide of manganese, artificially produced, is a brown powder. All the oxides of manganese are finally converted into this by strong ignition in the air. Each time it is heated it assumes a darker color, but its weight remains unaltered. It is insoluble in water, and does not alter vegetable colors. If ignited with chloride of ammonium, it is converted into the protochloride. When heated with concentrated hydrochloric acid, it dissolves to chloride with evolution of chlorine ($Mn_3O_4 + 4HCl = 3MnCl + Cl + 4HO$). On ignition with sulphur in a stream of hydrogen it is converted into sulphide (H. ROSE). On ignition in oxygen it is converted into sesquioxide (SCHNEIDER). On ignition in hydrogen it is converted into protoxide.

COMPOSITION.

Mn_3	82·50	72·05
O_4	32·00	27·95
	114·50	100·00

d. Binoxide of manganese is occasionally produced in analysis by exposing a concentrated solution of nitrate of protoxide of manganese to a gradually increased temperature. At 140° brown flakes separate, at 155° much nitrous acid is disengaged, and the whole of the manganese separates as anhydrous binoxide. It is brownish-black, and is deposited on the sides of the vessel, with metallic lustre. It is insoluble in weak nitric acid, but dissolves to a small amount in hot and concentrated nitric acid (DEVILLE). In hydrochloric acid it dissolves with evolution of chlorine, in concentrated sulphuric acid with liberation of oxygen. The binoxide is also sometimes obtained in the hydrated condition in analytical separations, thus when we precipitate a solution of protoxide with hypochlorite of soda, or, after addition of acetate of soda, with chlorine in the heat. The brownish-black flocculent precipitate thus obtained, contains alkali, from which it cannot be well freed by washing.

e. Sulphide of manganese, prepared in the wet way, generally forms a flesh-colored precipitate. I must make a few remarks with reference to its precipitation.* This is effected but incompletely if we add to a pure manganese solution only sulphide of ammonium, no matter whether it be colorless or yellow, while it is perfectly effected if chloride of ammonium be used in addition. A large quantity even of chloride of ammonium does not impede the precipitation. Ammonia in small quantity is not injurious, but in large quantity it interferes with complete precipitation, especially in the presence of polysulphide of ammonium (A. CLASSEN†). In all cases we must allow to stand at least 24 hours, and with very dilute solutions 48 hours, before filtering. Colorless or slightly yellow sulphide of ammonium is the most appropriate precipitant. In the presence of chloride of ammonium even a large excess of sulphide of ammonium is uninjurious. If the precipitation is conducted as directed, the manganese can be precipitated from solutions which contain only $\frac{1}{400000}$ of the protoxide. If the flesh-colored hydrated sulphide remains some time under the fluid, from which it was precipitated, it sometimes becomes converted into the green anhydrous sulphide.‡ This conversion is more likely to take place when a large excess of sulphide of ammonium has been used; heating favours it, chloride of ammonium hinders it. The conversion is occasionally rapid. The green sulphide thus obtained consists of eight-sided tables distinctly visible under the microscope (F. MUCK*). In acids (hydrochloric, sulphuric, acetic, &c.) the hydrate dissolves with evolution of sulphuretted hydrogen. If the precipitate, while still moist, is exposed to the air, or washed with water impregnated with air, it changes to brown, hydrated protosesquioxide of manganese being formed, together with a small portion of sulphate of protoxide of manganese. Hence in washing the hydrate we always add some sulphide of ammonium to the wash-water, and keep the filter as full as possible with the same. We guard against the filtrate running through turbid, by adding gradually decreasing quantities of chloride of ammonium to the wash-water (at last none). (Expt. No. 40.) On igniting the precipitate mixed with sulphur in a stream of hydrogen the anhydrous sulphide remains. If we have gently ignited during this process, the product is light green; if we have strongly ignited, it is dark-green to black. Neither the green nor the black sulphide attracts oxygen or water quickly from the air (H. ROSE). The anhydrous sulphide is also readily soluble in dilute acids.

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* Journ. f. prakt. Chem. 82, 265.

† Zeitschr. f. anal. Chem. 8, 370.

‡ Journ. f. prakt. Chem. 82, 268.

COMPOSITION.

Mn	27·5	63·22
S	16·0	36·78
	43·5	100·00

f. Anhydrous sulphate of protoxide of manganese, produced by exposing the crystallized salt to the action of heat, is a white, friable mass, readily soluble in water. It resists a very faint red heat; but upon exposure to a more intense red heat, it suffers more or less complete decomposition—oxygen, sulphurous acid, and anhydrous sulphuric acid being evolved, and protosesquioxide of manganese remaining behind. Ignited with sulphur in a stream of hydrogen it is transformed into sulphide (H. ROSE).

COMPOSITION.

MnO	35·50	47·02
SO_3	40·00	52·98
	75·50	100·00

g. Phosphate of manganese and ammonia.—GIBBS† says that this precipitate is insoluble in boiling water, but I have not found this to be the case. My results are that 1 part dissolves in 32092 parts of cold water, in 20122 parts boiling water, and 17755 parts of water containing $\frac{1}{10}$ of chloride of ammonium. It has the formula $2\,MnO,NH_4O,PO_5 + 2$ aq. It presents pale pink scales of pearly lustre, which sometimes turn reddish on the filter. On ignition it is converted into the pyrophosphate of manganese.

h. Pyrophosphate of manganese is the white residue left on the ignition of the preceding.

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* Zeitschr. f. Chem. N. F. 6, 6.

† SILLIM. Amer. Journ. (ii.) 44, 216.

COMPOSITION.

$2MnO$	35·50	33·33
PO_5	71·00	66·67
	106·50	100·00

§ 79.

3. Protoxide of Nickel.

Nickel is precipitated as HYDRATED PROTOXIDE, and as SULPHIDE. It is weighed in the form of PROTOXIDE, of METALLIC NICKEL, or of anhydrous PROTOSULPHATE.

a. Hydrated protoxide of nickel forms an apple-green precipitate, almost absolutely insoluble in water. When precipitated from a solution of the chloride or sulphate, it retains some of the acid even after long washing (TEICHMANN*). It is also very difficult to remove the last traces of alkali. It dissolves with some difficulty in ammonia and carbonate of ammonia, far more readily in the presence of an ammonia salt. From these solutions it is completely precipitated by excess of potassa or soda; application of heat promotes the precipitation. It is unalterable in the air; on ignition, it passes into anhydrous protoxide.

b. Protoxide of nickel is a dirty grayish-green powder. When obtained by heating the protonitrate to redness, it always contains some peroxide, and requires very strong and protracted ignition for conversion into the pure green protoxide (W. J. RUSSELL). It is insoluble in water, but readily soluble in hydrochloric acid. It does not affect vegetable colors. It suffers no variation of weight upon ignition with free access of air. Mixed with chloride of ammonium and ignited, it is reduced to metallic nickel (H. ROSE); it is also easily reduced by ignition in hydrogen or carbonic oxide.

COMPOSITION.

Ni	29·5	78·67
O	8·0	21·33
	37·5	100·00

c. Metallic nickel obtained by the reduction of the protoxide with hydrogen has the form of a gray powder, or if the heat has been very strong, and it has melted, it is lustrous and white like silver. It is unaltered in weight by ignition in hydrogen, when ignited in the air it is superficially oxidized. It is attracted by the magnet. It is dissolved slowly by hydrochloric acid and dilute sulphuric acid, and readily by moderately strong nitric acid.

d. Anhydrous protosulphate of nickel obtained by evaporating a solution of the chloride, nitrate, &c. with sulphuric acid is yellow, soluble in water to a green fluid. The hydrous salt may be rendered anhydrous without loss of acid by cautious heating in a platinum dish, but at low redness it begins to blacken at the edges and loses acid (F. GAUHE†).

e. Hydrated sulphide of nickel, prepared in the wet way, forms a black precipitate, insoluble in water. I must make some observations on its precipitation.* In order to precipitate the nickel from a pure solution completely and with ease, chloride of ammonium must be present, it is not enough to add sulphide of ammonium alone. A large quantity even of chloride of ammonium produces no injurious effect. In the presence of free ammonia, on the contrary, some nickel remains in solution. In this case, the supernatant fluid appears brown. As precipitant, colorless or light-yellow sulphide of ammonium containing no free ammonia should be used, a large excess must be avoided. If the directions given are adhered to—allowing to stand 48 hours—the nickel may be precipitated by means of sulphide of ammonium, from solutions containing only $\frac{1}{800000}$ of the oxide. As the precipitate is liable to take up oxygen from the air, being transformed into sulphate, a little sulphide of ammonium is mixed with the wash-water, to which also it is advisable to add chloride of ammonium (less and less—at last none); the filter should be kept full (Expt. No. 41). Brown filtrates, containing sulphide of nickel in solution, may be freed from the latter by acidulation with acetic acid, and boiling some time. The sulphide falls down, and may now be filtered off. It is very sparingly soluble in concentrated acetic acid, somewhat more soluble in hydrochloric acid. It is more readily soluble still in nitric acid, but its best solvent is nitrohydrochloric acid. It loses its water upon the application of a red heat; when ignited in the air, it is transformed into a basic compound of protoxide of nickel with sulphuric acid. Mixed with sulphur and ignited in a stream of hydrogen, a fused mass remains, of pale-yellow color and metallic lustre. This consists of Ni_2S, but its composition is not perfectly constant (F. GAUHE†). If a solution of a neutral salt of nickel is heated with excess of hyposulphite of soda in a sealed tube to 120°, the whole of the nickel will be thrown down in the course of half an hour as sulphide [$NiCl + 2(NaO,S_2O_2) = NiS + NaCl + NaO,S_3O_5$]. The sulphide thus obtained is black, unalterable in the air, can be easily washed, is barely attacked by hydrochloric acid or dilute sulphuric acid, and may be converted into protosulphate by dissolving in nitric acid, and evaporating the solution with sulphuric acid (W. GIBBS‡).

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* Annal. d. Chem. u. Pharm. 156, 17.

† Zeitschr. f. anal. Chem. 4, 190.

§ 80.

4. PROTOXIDE OF COBALT.

Cobalt is weighed in the PURE METALLIC state, or as PROTOSULPHATE. Besides the properties of these substances, we have to study also those of the HYDRATED PROTOXIDE, of the SULPHIDE, and of the NITRITE of SESQUIOXIDE of COBALT AND POTASSA.

a. Hydrated protoxide of cobalt.—Upon precipitating a solution of protoxide of cobalt with potassa, a blue precipitate (a basic salt) is formed at first, which, upon boiling with potassa in excess, excluded from contact of air, changes to light-red hydrate; if, on the contrary, this process is conducted with free access of air, the precipitate becomes discolored, and finally black, part of the hydrated protoxide being converted into hydrated sesquioxide. But the hydrate, prepared in this way, retains always a certain quantity of the acid, and, even after the most thorough washing with hot water, also a small amount of the alkaline precipitant. The latter, however, is not enough to spoil the accuracy of the results (H. ROSE, F. GAUHE*). Hydrated protoxide of cobalt is insoluble in water, and also in dilute potassa; it is somewhat soluble in very concentrated potassa, and readily in ammonia salts. When dried in the air, it absorbs oxygen, and acquires a brownish color. By strong ignition it is converted into protoxide (even if some protosesquioxide had formed from boiling or drying in the air); if cooled with exclusion of air, as in a current of carbonic acid, pure light-brown protoxide will be left; if cooled, on the contrary, with access of air, the protoxide is more or less changed to black protosesquioxide (W. J. RUSSELL†). By ignition in a current of hydrogen, metallic cobalt is left, from which any traces of alkali may now be almost completely removed by boiling water.

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* Journ. f. prakt. Chem. 82, 257.

† Zeitschr. f. anal. Chem. 4, 191.

‡ *Ib.* 3, 389.

b. The *metallic cobalt* obtained according to *a*, or by igniting the chloride or the protosesquioxide (produced by igniting the nitrate) in hydrogen is a grayish-black powder, which is attracted by the magnet, and is more difficultly fusible than gold. If the reduction has been effected at a faint heat, the finely divided metal burns in the air to protosesquioxide of cobalt, which is not the case if the reduction has been effected at an intense heat. Cobalt does not decompose water, either at the common temperature, or upon ebullition—except sulphuric acid be present, in which case decomposition will ensue. Heated with concentrated sulphuric acid, it forms sulphate of protoxide of cobalt, with evolution of sulphurous acid. In nitric acid it dissolves readily to nitrate of protoxide of cobalt.

c. Sulphide of cobalt, produced in the wet way, forms a black precipitate, insoluble in water, alkalies, and alkaline sulphides. With regard to its precipitation,‡—this is effected but slowly and imperfectly by sulphide of ammonium alone, in the presence of chloride of ammonium however, it takes place quickly and completely. Free ammonia is not injurious; it is all one, whether colorless or yellow sulphide of ammonium is employed. If the directions given are observed, cobalt may be precipitated from a solution containing no more than $\frac{1}{800000}$ of the protoxide. In the moist condition, exposed to the air, it oxidizes to sulphate. In washing it, therefore, water containing sulphide of ammonium is employed, and the filter is kept full. It is advisable also to mix a little chloride of ammonium with the wash-water, but its quantity should be gradually decreased, and the last water used must contain none. It is but sparingly soluble in acetic acid and in dilute mineral acids, more readily in concentrated mineral acids, and most readily in warm nitro-hydrochloric acid. Mixed with sulphur and ignited in a stream of hydrogen, we obtain a product which varies in composition according to the temperature employed. The residue is therefore not suited for the determination of cobalt (H. ROSE). By heating a solution of cobalt with excess of hyposulphite of soda in a sealed tube at 120° for one hour, all the cobalt is precipitated as a heavy black sulphide, unalterable in the air, easily washed, insoluble in dilute hydrochloric and sulphuric acids (W. GIBBS§). It may be converted into sulphate by heating in the air, moistening with nitric acid, evaporating with sulphuric acid and igniting.

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* Zeitschr. f. anal. Chem. 4, 54.

† Journ. Chem. Soc. (2) 1, 51.

‡ Journ. f. prakt. Chem. 82, 262.

§ Zeitschr. f. anal. Chem. 3, 390.

d. Sulphate of protoxide of cobalt crystallizes, in combination with 7 aq., slowly in oblique rhombic prisms of a fine red color. The crystals yield the whole of the water, at a moderate heat, and are converted into a rose-colored anhydrous salt, which bears the application of a low red heat without losing acid. At a stronger heat the edges become black and some sulphuric acid escapes (F. GAUHE*). It dissolves rather difficultly in cold, but more readily in hot water.

COMPOSITION.

CoO	37·5	48·39
SO_3	40·0	51·61
	77·5	100·00

•*e. Nitrite of sesquioxide of cobalt and potassa.*—If a solution of a cobalt salt (not too dilute) is mixed with excess of potassa and then with acetic acid till the precipitate is redissolved, and a concentrated solution of nitrite of potassa previously acidified with acetic acid is added, first a dirty-brownish precipitate forms which gradually turns yellow and crystalline, especially on the application of a gentle heat (N. W. FISCHER†). The precipitate dried at 100° consists of $Co_2O_3,2NO_3 + 3\,KO,NO_3 + 2HO$ (A. STROMEYER‡). It is decidedly soluble in water, less in acetate of potassa whether neutral or acidified with acetic acid, not in acetate of potassa to which some nitrite of potassa has been added, not in nitrite of potassa, nor in alcohol of 80 per cent. On washing with water or solution of acetate of potassa, unless nitrite of potassa is added, nitric oxide is constantly evolved in small quantities. It is decomposed with separation of brown sesquioxide of cobalt, with difficulty by solution of potassa, with ease by soda or baryta. On being moistened with sulphuric acid and ignited (finally with addition of carbonate of ammonia) it leaves $2(CoO,SO_3) + 3(KO,SO_3)$, but there is a difficulty in driving off all the excess of acid without decomposing the sulphate of cobalt. The yellow salt is soluble in hydrochloric acid, potassa precipitates the whole of the cobalt from this solution as hydrated protoxide or protosesquioxide.

§ 81.

5. PROTOXIDE OF IRON; and 6. SESQUIOXIDE OF IRON.

Iron is usually weighed in the form of SESQUIOXIDE, occasionally as SULPHIDE. We have to study also the HYDRATED SESQUIOXIDE, the SUCCINATE OF THE SESQUIOXIDE, the ACETATE OF THE SESQUIOXIDE, and the FORMATE OF THE SESQUIOXIDE.

a. Hydrated sesquioxide of iron, recently prepared, is a reddish-brown precipitate, insoluble in water, in dilute alkalies, and in ammoniacal salts, but readily soluble in acids; it shrinks very greatly on drying. When dry, it presents a brown, hard mass, with shining conchoidal fracture. If the precipitant alkali is not used in excess, the precipitate contains basic salt; on the other hand, if the alkali has been used in excess, a portion of it is invariably carried down in combination with the sesquioxide of iron,—on which account ammonia alone can properly be used in analysis for this purpose. Under certain circumstances, for instance, by protracted heating of a solution of acetate of sesquioxide of iron on the water-bath (which turns the solution from blood-red to brick-red, and makes it appear turbid by reflected light), and subsequent addition of some sulphuric acid or salt of an alkali, a reddish-brown hydrate is produced, which is insoluble in cold acids, even though concentrated, and is not attacked even by boiling nitric acid (L. PEAN DE ST. GILLES*).

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* Zeitschr. f. anal. Chem. 4, 55.

† Pogg. Ann. 72, 477.

‡ Ann. d. Chem. u. Pharm. 96, 218.

Closely allied to the hydrated sesquioxide of iron are the highly basic salts obtained by mixing dilute cold solutions of sesquioxide of iron, best the sesquichloride, with much chloride of ammonium, cautiously adding carbonate of ammonia till the fluid on standing in the cold instead of becoming clear turns more turbid if anything, and then boiling. The precipitates, thus produced in the fluid which still retains its acid reaction, contain the whole of the iron present and play an important part in analytical separations. They should be washed with boiling water containing chloride of ammonium, being soluble to a slight extent in pure water. They are not suitable for ignition, as sesquichloride of iron might occasionally escape from them.

b. The hydrated sesquioxide of iron is, upon ignition, converted into the *anhydrous sesquioxide*. If the hydrate has been superficially dried only, the violent escape of steam from the lumps is likely to occasion loss; but if the hydrate has been dried as much as possible by suction and still remains moist, it may be ignited without fear of loss. Pure sesquioxide of iron, when placed upon moist reddened litmus-paper, does not change the color to blue. It dissolves slowly in dilute, but more rapidly in concentrated hydrochloric acid; the application of a moderate degree of heat effects this solution more readily than boiling. With a mixture of 8 parts concentrated sulphuric acid and 3 parts water, it behaves in the same manner as alumina. The weight of the sesquioxide does not vary upon ignition in the air; when ignited with chloride of ammonium, sesquichloride of iron escapes. Ignition with charcoal, in a closed vessel, reduces it more or less. Strongly ignited with sulphur in a stream of hydrogen, it is transformed into protosulphide.

COMPOSITION.

Fe_2	56	70·00
O_3	24	30·00
	80	100·00

c. Sulphide of iron, produced in the wet way, forms a black precipitate. The following facts are to be noticed with regard to its precipitation.† Sulphide of ammonium used alone, whether colorless or yellow, precipitates pure neutral solutions of protoxide of iron, but slowly and imperfectly. Chloride of ammonium acts very favourably; a large excess even is not attended with inconvenience. Ammonia has no injurious action. It is all the same whether the sulphide of ammonium be colorless or light yellow. If the directions given are observed, iron may be precipitated by means of sulphide of ammonium from solutions containing only $\frac{1}{1800000}$ of the protoxide. In such a case, however, it is necessary to allow to stand forty-eight hours. Since the precipitate rapidly oxidizes in contact with air, sulphide of ammonium is to be added to the wash-water, and the filter kept full. It is well also to mix a little chloride of ammonium with the wash-water, but the quantity should be continually reduced, and the last water used should contain none. In mineral acids, even when very dilute, the hydrated sulphide dissolves readily. Mixed with sulphur, and strongly ignited in a stream of hydrogen, anhydrous protosulphide remains (H. Rose).

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* Journ. f. prakt. Chem. 66, 137.

† *Ib.* 82, 268.

COMPOSITION.

Fe	28	63·64
S	16	36·36
	44	100·00

d. When a neutral solution of a salt of sesquioxide of iron is mixed with a neutral solution of an alkaline succinate, a cinnamon-colored precipitate of a brighter or darker tint is formed; this is *succinate of sesquioxide of iron* ($Fe_2O_3,C_8H_4O_6$). It results from the nature of this precipitate, that its formation must set free an equivalent of acid (of succinic acid, if the succinate of ammonia is used in excess); *e.g.*, $2(Fe_2O_3,3SO_8) + 3(2NH_4O,C_8H_4O_6) + 2HO = 2(Fe_2O_3,C_8H_4O_6) + 6(NH_4O,SO_3) + 2HO,C_8H_4O_6$. The free succinic acid does not exercise any perceptible solvent action upon the precipitate in a cold and highly dilute solution, but it redissolves the precipitate a little more readily in a warm solution. The precipitate must therefore be filtered cold, if we want to guard against re-solution. Formerly the precipitate was erroneously supposed to consist of a neutral salt, decomposable by hot water into an insoluble basic and a soluble acid compound. Succinate of sesquioxide of iron is insoluble in cold, and but sparingly soluble in hot water. It dissolves readily in mineral acids. Ammonia, especially if warm, deprives it of the greater portion of its acid, leaving compounds similar to the hydrated sesquioxide of iron, which contain from 18 to 30 eq. Fe_2O_8 for 1 eq. $C_8H_4O_6$ (Döpping).

e. If to a solution of a salt of sesquioxide of iron carbonate of soda be added in the cold, till the fluid contains no more free acid, and in consequence of the formation of basic salt has become deep red, but remains still perfectly clear, and then acetate of soda be poured in and the mixture boiled, the whole of the iron will be precipitated as *basic acetate of sesquioxide*. The success of this operation depends on the iron solution being sufficiently dilute, the free acid sufficiently neutralized, and the acetate of soda in sufficient quantity. The duration of the boiling is of small importance; if the proportions have been properly hit one boiling up is enough. It need hardly be mentioned that the iron must previously be all converted into sesquioxide. Instead of carbonate and acetate of soda the corresponding salts of ammonia may be used. The precipitate may usually be filtered off and washed without any iron passing into the filtrate; sometimes, however, the reverse is the case. I should recommend not to boil longer than necessary to precipitate, to filter hot, and to use boiling wash-water mixed with some acetate of soda or of ammonia; this gives rise to no inconvenience, since the precipitate is usually redissolved in hydrochloric acid, and this solution finally precipitated with ammonia.

f. Instead of the acetate of soda or ammonia used in *e*, the corresponding formates may be used. The *basic formate of sesquioxide of iron* here obtained is more easily washed than the basic acetate (F. SCHULZE*).

BASES OF THE FIFTH GROUP.

§ 82.

1. OXIDE OF SILVER.

Silver may be weighed in the METALLIC state, as CHLORIDE, SULPHIDE, or CYANIDE.

a. Metallic silver, obtained by the ignition of salts of silver with organic acids, &c., is a loose, white, glittering mass of metallic lustre; but, when obtained by reducing chloride of silver, &c., in the wet way, by zinc, it is a dull gray powder. It fuses at about 1000°. Its weight is not altered by moderate ignition. It may, however, be distilled by the heat of the oxyhydrogen flame (CHRISTOMANOS†). It dissolves readily and completely in dilute nitric acid.

b. Chloride of silver, recently precipitated, is white and curdy. On shaking, the large spongy flocks combine with the smaller particles, so that the fluid becomes perfectly clear. This result is, however, only satisfactorily effected when the flocks have been recently precipitated in presence of excess of silver solution (compare G. J. MULDER‡). Chloride of silver is in a very high degree insoluble in water, and in dilute nitric acid; strong nitric acid, on the contrary, does dissolve a trace. Hydrochloric acid, especially if concentrated and boiling, dissolves it very perceptibly. According to PIERRE, 1 part of chloride of silver requires for solution 200 parts of strong hydrochloric acid and 600 parts of a dilute acid, composed of 1 part strong acid and 2 parts water. On sufficiently diluting such a solution with cold water the chloride of silver falls out so completely that the filtrate is not colored by sulphuretted hydrogen. Chloride of silver is insoluble, or very nearly so in concentrated sulphuric acid; in the dilute acid it is as insoluble as in water. In a solution of tartaric acid chloride of silver dissolves perceptibly on warming; on cooling, however, the solution deposits the whole, or, at all events, the greater part of it. Aqueous solutions of chlorides (of sodium, potassium, ammonium, calcium, zinc, &c.) all dissolve appreciable quantities of chloride of silver, especially if they are hot and concentrated. On sufficient dilution with cold water the dissolved portion separates so completely that the filtrate is not colored by sulphuretted hydrogen. The solutions of alkaline and alkaline earthy nitrates also dissolve a little chloride of silver. The solubility in the cold is trifling; in the heat, on the contrary, it is very perceptible. A strong solution of nitrate of silver dissolves it slightly, especially in the heat; but I have found it insoluble in a moderately dilute cold solution of nitrate of lead. The action of salts of mercury upon it is remarkable. When well washed and treated with a very dilute solution of chloride of mercury, it becomes white if previously a little blackened by light, is easily diffused in the fluid, and is but tardily deposited. This depends upon the mercury salt being taken up; if the silver salt is washed the mercury salt will be removed. Nitrate of mercury acts in a similar way, but a certain quantity of silver passes at the same time into solution. Chloride of silver is much more difficultly dissolved by acetate of mercury than by the nitrate of mercury; therefore if you have a solution of nitrate of mercury containing chloride of silver, if the mercury salt is not present in enormous quantity, the silver may be almost absolutely thrown down by addition of an alkaline acetate (H. Debray*). Solutions of potash and soda decompose chloride of silver, even at the ordinary temperature, more readily on boiling; oxide of silver separates, and chloride of the alkali metal is formed. Solution of carbonate of soda or of potash decomposes chloride of silver only very imperfectly even on boiling; after long boiling decided traces of chlorine are found in the filtrate. Chloride of silver dissolves readily in aqueous ammonia, and also in the solution of cyanide of potassium and that of hyposulphite of soda. According to Wallace and Lamont† 1 part of chloride of silver dissolves in 12·88 parts of strong aqueous ammonia of ·89 sp. gr. Under the influence of light the chloride of silver soon changes to violet, finally black, losing chlorine, and passing partly into Ag_2Cl. The change is quite superficial, but the loss of weight resulting is very appreciable (Mulder, *op. cit.* p. 21). If chloride of silver that has become violet or black from the influence of light be treated with aqueous ammonia, it dissolves with separation of a very small quantity of metallic silver, Ag_2Cl gives $AgCl$ and Ag (Wittstein). On long contact (say for 24 hours) with water, especially of 75°, chloride of silver, although removed from the influence of light, becomes gray, and, it appears, decomposed; the precipitate is found to contain oxide of silver, and the water hydrochloric acid (Mulder). On digestion with excess of solution of bromide or iodide of potassium, the chloride of silver is completely transformed into bromide or iodide of silver, as the case may be (Field‡). On drying, chloride of silver becomes pulverulent; on heating it turns yellow; at 260° it fuses to a transparent yellow fluid; at a very high heat it volatilizes without decomposition. On cooling after fusion it presents a colorless or pale yellowish mass. Fused in chlorine gas, it absorbs some chlorine; on cooling, this escapes, but not completely. If it is to be completely expelled, and, in very delicate experiments this must be done, we pass carbonic acid before allowing to cool (Stas§). Ignition with charcoal fails to effect its reduction to the metallic state; but it may be readily so reduced in a current of hydrogen, carburetted hydrogen, or carbonic oxide.

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* Chem. Centralblatt, 1861, 3.

† Zeitschr. f. anal. Chem. 7, 299.

‡ Die Silberprobirmethode, translated into German by D. Chr. Grimm, pp. 19 and 311. Leipzig: J. J. Weber. 1859.

COMPOSITION.

Ag	107·93	75·27
Cl	35·46	24·73
	143·39	100·00

c. ***Sulphide of silver***, prepared in the wet way, is a black precipitate, insoluble in water, dilute acids, alkalies, and alkaline sulphides. It is

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[*] Zeitschr. f. Chem. 13, 348.

[†] Chem. Gaz. 1859, 137.

[‡] Quart. Journ. Chem. Soc. 10, 234.

[§] Recherches sur les rapports réciproques des poids atomiques, p. 37. Bruxelles, 1860. The loss of weight which about 100 grm. chloride of silver suffered, by the expulsion of the absorbed chlorine, was from 7 to 13 mgrm.

unalterable in the air; after being allowed to subside, it is filtered and washed with ease, and may be dried at 100° without decomposition. It dissolves in concentrated nitric acid, with separation of sulphur. Solution of cyanide of potassium dissolves it with difficulty, if it was precipitated from a very dilute solution with less difficulty; the quantity of cyanide of potassium, too, has great influence on the effect. For instance, if cyanide of silver is dissolved in a bare sufficiency of cyanide of potassium and sulphuretted hydrogen, or sulphide of ammonium is added, sulphide of silver is thrown down; if, on the other hand, a large excess of cyanide of potassium is present, no precipitate will be produced. If sulphide of silver is dissolved in a concentrated solution of cyanide of potassium, it will generally separate at once on addition of much water (BECHAMP*). Ignited in a current of hydrogen, it passes readily and completely into the metallic state (H. ROSE).

COMPOSITION.

Ag	107·93	87·09
S	16·00	12·91
	123·93	100·00

d. Cyanide of silver, recently thrown down, forms a white curdy precipitate insoluble in water and dilute nitric acid, soluble in cyanide of potassium and also in ammonia; exposure to light fails to impart the slightest tinge of black to it; it may be dried at 100° without decomposition. Upon ignition, it is decomposed into cyanogen, which escapes, and metallic silver, which remains, mixed with a little paracyanide of silver. By boiling with a mixture of equal parts of sulphuric acid and water, it is, according to GLASSFORD and NAPIER, dissolved to sulphate of silver, with liberation of hydrocyanic acid.

COMPOSITION.

Ag	107·93	80·56
C_2N	26·04	19·44
	133·97	100·00

§ 83.

2. OXIDE OF LEAD.

Lead is weighed as OXIDE, SULPHATE, CHROMATE, CHLORIDE, and SULPHIDE. Besides these compounds, we have also to study the CARBONATE and the OXALATE.

a. Neutral carbonate of lead forms a heavy, white, pulverulent precipitate. It is but very slightly soluble in perfectly pure (boiled) water, one part requiring 50550 parts (see Expt. No. 42, *a*); but it dissolves somewhat more readily in water containing ammonia and ammoniacal salts (comp. Expt. No. 42, *b* and *c*), and also in water impregnated with carbonic acid. It loses its carbonic acid when ignited.

b. Oxalate of lead is a white powder, very sparingly soluble in

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[*] Journ. f. prakt. Chem. 60, 64.

water. The presence of ammonia salts slightly increases its solubility (Expt. No. 43). When heated in close vessels, it leaves suboxide of lead; but when heated with access of air, the yellow oxide.

c. Oxide of lead, produced by igniting the carbonate or oxalate, is a lemon-yellow powder, inclining sometimes to a reddish-yellow, or to a pale yellow. When this yellow oxide of lead is heated, it assumes a brownish-red color, without the slightest variation of weight. It fuses at an intense red heat. Ignition with charcoal reduces it. When exposed to a white heat, it rises in vapor. Placed upon moist red litmus paper, it changes the color to blue. When exposed to the air, it slowly absorbs carbonic acid. Mixed with chloride of ammonium and ignited, it is converted into chloride of lead. Oxide of lead in a state of fusion readily dissolves silicic acid and the earthy bases with which the latter may be combined.

COMPOSITION.

Pb	103·50	92·83
O	8·00	7·17
	111·50	100·00

d. Sulphate of lead is a heavy white powder. It dissolves, at the common temperature, in 22800 parts of pure water (Expt. 44[*]); it is less soluble in water containing sulphuric acid (one part requiring 36500 parts—Expt. No. 45); it is far more readily soluble in water containing ammoniacal salts; from this solution it may be precipitated again by adding sulphuric acid in excess (Expt. No. 46). It is almost entirely insoluble in alcohol and spirit of wine. Of the salts of ammonia, the nitrate, acetate, and tartrate are more especially suited to serve as solvents for sulphate of lead: the two latter salts of ammonia are made strongly alkaline by addition of ammonia, previous to use (WACKENRODER). Sulphate of lead dissolves in concentrated hydrochloric acid, upon heating. In nitric acid it dissolves the more readily, the more concentrated and hotter the acid; water fails to precipitate it from its solution in nitric acid; but the addition of a copious amount of dilute sulphuric acid causes its precipitation from this solution. The more nitric acid the solution contains, the more sulphuric acid is required. It dissolves sparingly in concentrated sulphuric acid, and the dissolved portion precipitates again upon diluting with water (more completely upon addition of alcohol). A moderately concentrated solution of hyposulphite of soda dissolves sulphate of lead completely even if cold, more readily if warmed; on boiling, the solution becomes black, from separation of a small quantity of sulphide of lead (J. LÖWE[†]). The solutions of carbonates and bicarbonates of the alkalies convert sulphate of lead, even at the common temperature, completely into carbonate of lead. The solutions of the carbonates, but not those of the bicarbonates, dissolve some oxide of lead in this process (H. ROSE[‡]). Sulphate of lead dissolves readily in hot solutions of potassa or soda. It is unalterable in the air, and at a gentle red heat; when exposed to a full red heat, it fuses without decomposition (Expt. No. 47), provided always reducing gases be completely excluded—for, if this is not the case, the weight will continually diminish, owing to reduction to sulphide (ERDMANN*). At a white heat the whole of the sulphuric acid gradually escapes. (BOUSSINGAULT†). When it is ignited with charcoal, sulphide of lead is formed at first; if the heat be raised, this sulphide reacts on undecomposed sulphate, metallic lead and sulphurous acid being produced. Fusion with cyanide of potassium reduces the whole of the lead to the metallic state. Sulphate of lead mixed with sulphur and exposed to intense ignition in a current of hydrogen, yields the sulphide, but loss can scarcely be avoided, compare *f.*

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[*] According to G. F. RODWELL 1 part dissolves in 31696 parts water at 15° (Chem. News, 1866, 50).

[†] Journ. f. prakt. Chem. 74, 348.

[‡] Pogg. Annal. 95, 426.

COMPOSITION.

PbO	111·50	73·60
SO_3	40·00	26·40
	151·50	100·00

e. Chloride of lead obtained by precipitation is a white crystalline powder. It separates in needles from a hot solution containing a certain quantity of hydrochloric acid; occasionally it presents wedge-shaped crystals, or when separated from a strong hydrochloric solution, hexagonal tables. At 17°·7 water dissolves ·946 per cent.; a fluid containing 15 per cent. of hydrochloric acid of 1·162 sp. gr. dissolves ·090; a fluid containing 20 per cent. acid dissolves ·111 per cent.; a fluid containing 80 per cent. acid dissolves 1·498 per cent. Pure hydrochloric acid of the above strength dissolves 2·900 per cent. (J. CARTER BELL‡). Chloride of lead is less soluble in water containing nitric acid than in water (1 part requires 1636 parts, BISCHOF). It is extremely sparingly soluble in spirit of wine of 70 to 80 per cent., and altogether insoluble in absolute alcohol. It is unalterable in the air. It fuses at a temperature below red heat, without loss of weight. When exposed to a higher temperature, with access of air, it volatilizes slowly, being partially decomposed: chlorine gas escapes, and a mixture of oxide and chloride of lead remains.

COMPOSITION.

Pb	103·50	74·48
Cl	35·46	25·52
	138·96	100·00

f. Sulphide of lead, prepared in the wet way, is a black precipitate, insoluble in water, dilute acids, alkalies, and alkaline sulphides. In precipitating it from a solution containing free hydrochloric acid, it is necessary to dilute plentifully, otherwise the precipitation will be incomplete. Even if a fluid only contain 2·5 per cent. HCl, the whole of the lead will not be precipitated (M. MARTIN§). It is unalterable in the air; it cannot be dried at 100° without decomposition. According to H. Rose it increases perceptibly in weight by oxidation; in the case of long-protracted drying even becoming a few per-cents heavier.[*] I have confirmed his statement (see Expt. No. 48). If sulphide of lead mixed with sulphur is heated gently in a current of hydrogen, so that the lower quarter of the crucible is red hot, sulphide of lead is left without loss of weight. By continuing a gentle heat the weight gradually diminishes, by strong ignition the loss is rapid. This loss is partly owing to volatilization of sulphide of lead, but mainly to escape of sulphur in the form of sulphuretted hydrogen and formation of Pb_2S, or even of lead (A. Souchay[†]). It dissolves in concentrated hot hydrochloric acid, with evolution of sulphuretted hydrogen. In moderately strong nitric acid, sulphide of lead dissolves, upon the application of heat, with separation of sulphur;—if the acid is rather concentrated, a small portion of sulphate of lead is also formed. Fuming nitric acid acts energetically upon sulphide of lead, and converts it into sulphate without separation of sulphur.

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* Journ. f. prakt. Chem. 62, 381.

† Zeitschr. f. anal. Chem. 7, 244.

‡ Journ. Chem. Soc. (2) 6, 355.

§ Journ. f. prakt. Chem. 67, 374.

COMPOSITION.

Pb	103·50	86·61
S	16·00	13·39
	119·50	100·00

g. For the composition and properties of *chromate of lead* see *Chromic acid*, § 93.

§ 84.

3. Suboxide of Mercury; and 4. Oxide of Mercury.

Mercury is weighed either in the METALLIC STATE, as SUBCHLORIDE, or as SULPHIDE, or occasionally as OXIDE.

a. Metallic mercury is liquid at the common temperature; it has a tin-white color. When pure, it presents a perfectly bright surface. It is quite unalterable in the air at the common temperature. It boils at 360°. It evaporates, but very slowly, at the ordinary temperature of summer. Upon long-continued boiling with water, a small portion of mercury volatilizes, and traces escape along with the aqueous vapor, whilst a very minute proportion remains suspended (not dissolved) in the water (comp. Expt. No. 49). This suspended portion of mercury subsides completely after long standing. When mercury is precipitated from a fluid, in a very minutely divided state, the small globules will readily unite to a large one if the mercury be perfectly pure; but even the slightest trace of extraneous matter, such as fat, &c., adhering to the mercury will prevent the union of the globules. Mercury does not dissolve in hydrochloric acid, even in concentrated; it is barely soluble in dilute cold sulphuric acid, but dissolves readily in nitric acid.

b. Subchloride of mercury, prepared in the wet way, is a heavy white powder. It is almost absolutely insoluble in cold water; in boiling water it is gradually decomposed, the water taking up chlorine and mercury; upon continued boiling, the residue acquires a gray color. Highly dilute hydrochloric acid fails to dissolve it at the common temperature, but dissolves it slowly at a higher temperature; upon ebullition, with access of air, the whole of the subchloride is gradually dissolved: the solution contains chloride of mercury ($Hg_2Cl + HCl + O = 2HgCl + HO$). When acted upon by boiling concentrated hydrochloric acid, it is rather speedily decomposed into mercury, which remains undissolved, and chloride of mercury, which dissolves. Boiling nitric acid dissolves it to chloride and nitrate of mercury. Chlorine water and nitrohydrochloric acid dissolve it to chloride, even in the cold. Solutions of chloride of ammonium, chloride of sodium, and chloride of potassium, decompose it into metallic mercury and chloride of mercury, which latter dissolves; in the cold, this decomposition is but slight, heat promotes the action. It is soluble in hot solution of subnitrate of mercury, and still more in that of nitrate of mercury; on cooling it crystallizes out almost completely (DEBRAY*). It does not affect vegetable colors; it is unalterable in the air, and may be dried at 100°, without loss of weight; when exposed to a higher degree of heat, though still below redness, it volatilizes completely, without previous fusion.

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[*] Pogg. Annal. 91, 110; and 110, 134.

[†] Zeitschr. f. anal. Chem. 4, 63.

COMPOSITION.

Hg_2	200·00	84·94
Cl	35·46	15·06
	235·46	100·00

c. Sulphide of mercury, prepared in the wet way, is a black powder, insoluble in water. Dilute hydrochloric acid, and dilute nitric acid fail to dissolve it, hot concentrated nitric acid scarcely attacks it, boiling hydrochloric acid has no action on it. By prolonged heating with red fuming nitric acid it is finally converted into a white compound $2HgS + HgO,NO_5$, which is insoluble or barely soluble in nitric acid. It dissolves readily in nitrohydrochloric acid. From a solution of chloride of mercury, containing much free hydrochloric acid, the whole of the metal cannot be precipitated as sulphide by means of sulphuretted hydrogen, until the solution is properly diluted. Should such a solution be very concentrated, subchloride of mercury and sulphur are precipitated (M. MARTIN†). Solution of potassa, even boiling, fails to dissolve it. It dissolves in sulphide of potassium, but readily only in presence of free alkali. It is insoluble in sulphide of potassium and hydrogen and in the corresponding sodium compound, and is therefore precipitated from its solution in sulphide of potassium or sodium by sulphuretted hydrogen or by sulphide of ammonium and hydrogen (C. BARFOED‡). Small but distinctly perceptible traces dissolve on cold digestion with yellowish or yellow sulphide of ammonium, but after hot digestion it is scarcely possible to detect any traces in solution.§ Cyanide of potassium, and sulphite of soda do not dissolve it. On account of the solubility of sulphide of mercury in sulphide of potassium, it is impossible to precipitate mercury by means of sulphide of ammonium completely from solutions containing hydrate or carbonate of potassa or soda. Such solutions may occur, for instance, when a solution of chloride of mercury contains much chloride of potassium, or chloride of sodium, for, in this case, no oxide of mercury would be precipitated on the addition of potassa or soda (H. ROSE*). In the air it is unalterable, even in the moist state, and at 100°. When exposed to a higher temperature, it sublimes completely and unaltered.

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* Compt. Rend. 70, 995.

† Journ. f. prakt. Chem. 67, 376.

‡ Zeitschr. f. anal. Chem. 4, 436.

§ *Ib.* 3, 140.

COMPOSITION.

Hg	100·00	86·21
S	16·00	13·79
	116·00	100·00

d. Oxide of mercury, prepared in the dry way, is a crystalline brick-colored powder, which, when exposed to the action of heat, changes to the color of cinnabar, and subsequently to a violet-black tint. It bears a tolerably strong heat without decomposition; but when heated to incipient redness, it is decomposed into mercury and oxygen; perfectly pure oxide of mercury leaves no residue upon ignition. Its escaping fumes also should not redden litmus-paper. Water takes up a trace of oxide of mercury, acquiring thereby a very weak alkaline reaction. Hydrochloric or nitric acid dissolves it readily.

COMPOSITION.

Hg	100·00	92·59
O	8·00	7·41
	108·00	100·00

§ 85.

5. OXIDE OF COPPER.

Copper is usually weighed in the METALLIC STATE, or in the form of OXIDE, or of SUBSULPHIDE. Besides these forms, we have to examine the SULPHIDE, the SUBOXIDE, and the SUBSULPHOCYANIDE.

a. Copper, in the pure state, is a metal of a peculiar well-known color. It fuses only at a white heat. Exposure to dry air, or to moist air, free from carbonic acid, leaves the fused metal unaltered; but upon exposure to moist air impregnated with carbonic acid, it becomes gradually tarnished and coated with a film, first of a blackish-gray, finally of a bluish-green color. Precipitated finely divided copper, in contact with water and air, oxidizes far more quickly, especially at an elevated temperature. On igniting copper in the air, it oxidizes superficially to a varying mixture of oxide and suboxide. In hydrochloric acid, in the cold, it does not dissolve if air be excluded; in the heat it dissolves but slightly if the metal is in a compact state. Finely divided copper on the contrary dissolves slowly when heated with strong hydrochloric acid, hydrogen being evolved and subchloride of copper being formed (WELTZIEN†). Copper dissolves readily in nitric acid. In ammonia it dissolves slowly if free access is given to the air; but it remains insoluble if the air is excluded. Metallic copper brought into contact in a closed vessel with solution of chloride of copper in hydrochloric acid, or with an ammoniacal solution of oxide of copper, reduces the chloride to subchloride, or the oxide to suboxide, an equivalent of metal being dissolved for every equivalent of chloride or oxide.

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* Pogg. Annal. 110, 141.

† Ann. d. Chem. u. Pharm. 136, 109.

b. Oxide of copper.—If a dilute, cold, aqueous solution of a salt ot oxide of copper is mixed with solution of potassa or soda in excess, a light blue precipitate of hydrated oxide of copper (CuO,HO) is formed, which it is found difficult to wash. If the precipitate be left in the fluid from which it has been precipitated, it will, even at a summer heat, gradually change to brownish-black, yielding up the greater part of its water of hydration, and passing into $6CuO,HO$ (SOUCHAY). This transformation is immediate upon heating the fluid nearly to boiling. The fluid filtered off from the black precipitate is free from copper. It follows from this that the black precipitate is insoluble in dilute potassa. Concentrated potassa or soda on the contrary dissolves the hydrate, and on long warming even the black oxide (O. Löw[*]). The resulting blue solutions remain clear on boiling, even if mixed with some water; but if boiled after being much diluted the whole of the copper will separate as black oxide. If a solution of a salt of copper contains non-volatile organic substances, the addition of alkali in excess will, even upon boiling, fail to precipitate the whole of the copper as oxide. The hydrated oxide of copper ($6\,CuO,HO$) precipitated with potassa or soda from hot dilute solutions obstinately retains a portion of the precipitant; it may, however, be completely freed from this by washing with boiling water. The precipitated oxide after ignition, or the oxide prepared by decomposing the carbonate or nitrate by heat, is a brownish-black, or black powder, the weight of which remains unaltered even upon strong ignition over the gas- or spirit-lamp, provided all reducing gases be excluded (Expt. No. 50). If oxide of copper is exposed to a heat approaching the fusing point of metallic copper, it fuses, yields oxygen, and becomes Cu_5O_3 (FAVRE and MAUMENE). It is very readily reduced by ignition with charcoal, or under the influence of reducing gases; heated in the air for a long time, the reduced metallic copper re-oxidizes. Mixed with sulphur and ignited in a current of hydrogen, towards the end strongly, the oxide of copper passes into subsulphide (Cu_2S—H. ROSE). Oxide of copper, in contact with the atmosphere, absorbs water; less rapidly after being strongly ignited (Expt. No. 51). It is nearly insoluble in water; but it dissolves readily in hydrochloric acid, nitric acid, &c.; less readily in ammonia. It does not affect vegetable colors.

COMPOSITION.

Cu	31·70	79·85
O	8·00	20·15
	39·70	100·00

c. Sulphide of copper, prepared in the wet way, is a brownish-black, or black precipitate, almost absolutely insoluble in water.[†] When exposed to the air in a moist state, it acquires a greenish tint and the property of reddening litmus-paper, sulphate of copper being formed. Hence the sulphide must be washed with water containing sulphuretted hydrogen. It dissolves readily in boiling nitric acid, with separation of sulphur. Hydrochloric acid dissolves it with difficulty. This is the reason why sulphuretted hydrogen precipitates copper entirely from solutions which contain even a very large amount of free hydrochloric acid (GRUNDMANN*). Only when we dissolve a copper salt straight in pure hydrochloric acid of 1·1 sp. gr. does any copper remain unprecipitated (M. MARTIN†). It does not dissolve in solutions of potassa and of sulphide of potassium, particularly if these solutions be boiling; it dissolves perceptibly in colorless, and much more readily in hot yellow sulphide of ammonium. Cyanide of potassium dissolves the freshly precipitated sulphide readily and completely. Upon intense ignition in a current of hydrogen it is converted into pure Cu_2S.

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[*] Zeitschr. f. anal. Chem. 9, 463.

[†] In some experiments that I made when examining the Weilbach water, I found that about 950000 parts of water are required to dissolve 1 part of CuS.

d. If the blue solution which is obtained upon adding to solution of copper tartaric acid and then soda in excess, is mixed with solution of grape sugar or sugar of milk, and heat applied, an orange-yellow precipitate of hydrated suboxide of copper is formed, which contains the whole of the copper originally present in the solution, and after a short time, more particularly upon the application of a stronger heat, turns red, owing to the conversion of the hydrate into anhydrous suboxide (Cu_2O). The precipitate, which is insoluble in water, retains a portion of alkali with considerable tenacity. When treated with dilute sulphuric acid, it gives sulphate of copper which dissolves, and metallic copper which separates.

e. Subsulphocyanide of copper (Cu_2CyS_2) which is always formed when sulphocyanide of potassium is added to a solution of copper, mixed with sulphurous or hypophosphorous acid, is a white precipitate insoluble in water, as well as in dilute hydrochloric or sulphuric acid. Dried at 115°, the salt retains from 1 to 3 per cent. of water, which is driven off only by heating to incipient decomposition; it is, therefore, not well adapted for direct weighing. When ignited with sulphur, with exclusion of air, it changes to Cu_2S (RIVOT‡). When heated with hydrochloric acid and chlorate of potassa, or with sulphuric acid and nitric acid, it is dissolved and suffers decomposition. Solutions of potassa and soda separate hydrated suboxide of copper, with formation of sulphocyanide of the alkali metal.

f. Subsulphide of copper, produced by heating CuS in a current of hydrogen or Cu_2CyS_2 with sulphur, is a grayish-black crystalline mass, which may be ignited and fused without decomposition if the air is excluded.

COMPOSITION.

Cu_2	63·40	79·85
S	16·00	20·15
	79·40	100·00

§ 86.

6. OXIDE OF BISMUTH.

Bismuth is weighed as OXIDE, as METAL, or as CHROMATE (BiO_3, $2CrO_3$). Besides these compounds, we have to study here the BASIC

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* Journ. f. prakt. Chem. 73, 241.

† Ib. 67, 375.

‡ Ib. 62, 252.

CARBONATE, the BASIC NITRATE, the BASIC CHLORIDE, and the SULPHIDE.

a. Teroxide of bismuth, prepared by igniting the carbonate or nitrate, is a pale lemon-yellow powder which, under the influence of heat, assumes transiently a dark yellow or reddish-brown color. When heated to intense redness, it fuses, without alteration of weight. Ignition with charcoal, or in a current of carbonic oxide, reduces it to the metallic state. Fusion with cyanide of potassium also effects its complete reduction (H. ROSE*). It is insoluble in water, and does not affect vegetable colors. It dissolves readily in those acids which form soluble salts with it. When ignited with chloride of ammonium it gives metallic bismuth, the reduction being attended with deflagration.

COMPOSITION.

Bi	208	89·655
O_3	24	10·345
	232	100·000

b. Metallic bismuth is white, with a reddish tinge, moderately hard, brittle, with a tendency to crystallize. It fuses at 264°, and at a low white heat volatilizes. It does not oxidize in the air at the ordinary temperature, but with the cooperation of water it oxidizes slowly, more speedily on fusion. It dissolves in dilute nitric acid.

c. Carbonate of bismuth.—Upon adding carbonate of ammonia in excess to a solution of bismuth, free from hydrochloric acid, a white precipitate of carbonate of bismuth (BiO_3,CO_2) is immediately formed; part of this precipitate, however, redissolves in the excess of the precipitant. But if the fluid with the precipitate be heated before filtration, the filtrate will be free from bismuth. (Carbonate of potassa likewise precipitates solutions of bismuth completely; but the precipitate in this case invariably contains traces of potassa, which it is very difficult to remove by washing. Carbonate of soda precipitates solutions of bismuth less completely.) The precipitate is easily washed; it is practically insoluble in water, but dissolves readily, with effervescence, in hydrochloric and nitric acids. Upon ignition it leaves the oxide.

d. The *basic nitrate of bismuth*, which is obtained by mixing with water a solution of the nitrate containing little or no free acid, presents a white, crystalline powder. It cannot be washed with pure cold water without suffering a decided alteration. It becomes more basic, while the washings show an acid reaction, and contain bismuth. If the basic salt, however, be washed with cold water containing $\frac{1}{500}$ of nitrate of ammonia, no bismuth passes through the filter. The solution of nitrate of ammonia must not be warm. These remarks only apply in the absence of free nitric acid (J. LÖWE†). On ignition the basic nitrate passes into the oxide.

e. Basic chloride of bismuth, formed by adding much water to solution of bismuth containing hydrochloric acid or chloride of sodium, is a brilliant white powder ($2BiO_3,BiCl_3$ + aq.). It is insoluble in water, but dissolves in concentrated hydrochloric or nitric acid. Fused with cyanide of potassium it gives metallic bismuth.

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* Journ. f. prakt. Chem. 61, 188.

† *Ib.* 74, 341.

f. Chromate of bismuth ($BiO_3,2CrO_3$), which is produced by adding bichromate of potassa, slightly in excess, to a solution of nitrate of bismuth as neutral as possible, is an orange-yellow, dense, readily-subsiding precipitate, insoluble in water, even in presence of some free chromic acid, but soluble in hydrochloric acid and nitric acid. It may be dried at 100°–112° without decomposition (LÖWE*).

COMPOSITION.

BiO_3	232·00	69·78
$2CrO_3$ . . .	100·48	30·22
	332·48	100·00

g. Sulphide of bismuth, prepared in the wet way, is a brownish-black, or black precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphides, sulphite of soda and cyanide of potassium. In moderately concentrated nitric acid it dissolves, especially on warming, to nitrate, with separation of sulphur. Hence in precipitating bismuth from a nitric acid solution, care should be taken to dilute sufficiently. Hydrochloric acid impedes the precipitation by sulphuretted hydrogen only when a very large excess is present, and the fluid is quite concentrated. The sulphide does not change in the air. Dried at 100°, it continually takes up oxygen and increases slightly in weight; if the drying is protracted this increase may be considerable (Expt. No. 52). Fused with cyanide of potassium, it is completely reduced (H. ROSE). Reduction takes place more slowly by ignition in a current of hydrogen.

COMPOSITION.

Bi	208	81·25
S_3	48	18·75
	256	100·00

§ 87.

7. OXIDE OF CADMIUM.

Cadmium is weighed either as OXIDE or as SULPHIDE. Besides these substances, we have to examine CARBONATE OF CADMIUM.

a. Oxide of cadmium, produced by igniting the carbonate or nitrate, is a yellowish-brown or reddish-brown powder. The application of a white-heat fails to fuse, volatilize, or decompose it; it is insoluble in water, but dissolves readily in acids; it does not alter vegetable colors. Ignition with charcoal, or in a current of hydrogen, carbonic oxide, or carburetted hydrogen, reduces it readily, the metallic cadmium escaping in the form of vapor.

COMPOSITION.

Cd	56·00	87·50
O	8·00	12·50
	64·00	100·00

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* Journ. f. prakt. Chem. 67, 291.

b. Carbonate of cadmium is a white precipitate, insoluble in water and the fixed alkaline carbonates, and extremely sparingly soluble in carbonate of ammonia. It loses its water completely upon drying. Ignition converts it into oxide.

c. Sulphide of cadmium, produced in the wet way, is a lemon-yellow to orange-yellow precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphides, sulphite of soda, and cyanide of potassium (Expt. No. 53). It dissolves readily in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen. In precipitating, therefore, with sulphuretted hydrogen, a cadmium solution should not contain too much hydrochloric acid, and should be sufficiently diluted. The sulphide dissolves readily in dilute sulphuric acid on heating. It dissolves in moderately concentrated nitric acid, with separation of sulphur. It may be washed, and dried at 100° or 105°, without decomposition. Even on gentle ignition in a current of hydrogen, it volatilizes in appreciable amount (H. ROSE[*]), partially unchanged, partially as metallic vapor.

COMPOSITION.

Cd	56·00	77·78
S	16·00	22·22
	72·00	100·00

METALLIC OXIDES OF THE SIXTH GROUP.

§ 88.

1. TEROXIDE OF GOLD.

Gold is always weighed in the metallic state. Besides METALLIC GOLD, we have to consider the TERSULPHIDE.

a. Metallic gold, obtained by precipitation, presents a blackish-brown powder, destitute of metallic lustre, which it assumes, however, upon pressure or friction; when coherent in a compact mass, it exhibits the well-known bright yellow color peculiar to it. It fuses only at a white heat, and resists, accordingly, all attempts at fusion over a spirit-lamp. It remains wholly unaltered in the air and at a red heat, and is not in the slightest degree affected by water, nor by any simple acid. Nitrohydrochloric acid dissolves it to terchloride. Hot concentrated sulphuric acid containing a little nitric acid dissolves gold, especially if in a finely divided condition, to a yellow fluid, from which it is thrown down again by water (J. SPILLER[†]).

b. Tersulphide of gold.—When sulphuretted hydrogen is transmitted through a cold dilute solution of terchloride of gold, the whole of the gold separates as tersulphide (AuS_3), in form of a brownish-black precipitate. If this precipitate is left in the fluid, it is gradually transformed into metallic gold and free sulphuric acid. Upon transmitting sulphuretted hydrogen through a warm solution of terchloride of gold, a protosulphide (AuS) precipitates, with formation of sulphuric and hydrochloric acids.

$$(2AuCl_3 + 3HS + 4HO = 2AuS + 6HCl + HO,SO_3.)$$

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[*] Pogg. Annal. 110, 134.

[†] Chem. News, 14, 256.

The tersulphide is insoluble in water, hydrochloric acid, and nitric acid, but dissolves in nitrohydrochloric acid. The colorless sulphide of ammonium fails to dissolve it; but it dissolves almost entirely in the yellow sulphide of ammonium, and completely upon addition of potassa. It dissolves in potassa, with separation of gold. Yellow sulphide of potassium dissolves it completely. It dissolves in cyanide of potassium. Exposure to a moderate heat reduces it to the metallic state.

§ 89.

2. Binoxide of Platinum.

Platinum is invariably weighed in the METALLIC STATE; it is generally precipitated as BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM, or as BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM, rarely as BISULPHIDE OF PLATINUM.

a. Metallic platinum, produced by igniting the bichloride of platinum and chloride of ammonium, or the bichloride of platinum and chloride of potassium, presents the appearance of a gray, lustreless, porous mass (spongy platinum). The fusion of platinum can be effected only at the very highest degrees of heat. It remains wholly unaltered in the air, and in the most powerful furnaces. It is not attacked by water, or simple acids, and scarcely by aqueous solutions of the alkalies. Nitrohydrochloric acid dissolves it to bichloride.

b. The properties of *bichloride of platinum and chloride of potassium*, and those of *bichloride of platinum and chloride of ammonium*, have been given already in §§ 68 and 70 respectively.

c. Bisulphide of platinum.—When a concentrated solution of bichloride of platinum is mixed with sulphuretted hydrogen water, or when sulphuretted hydrogen gas is transmitted through a rather dilute solution of the bichloride, no precipitate forms at first; after standing some time, however, the solution turns brown, and finally a precipitate subsides. But if the mixture of solution of bichloride of platinum with sulphuretted hydrogen in excess, is gradually heated (finally to ebullition), the whole of the platinum separates as bisulphide (free from any admixture of bichloride). The bisulphide of platinum is insoluble in water and in simple acids; but it dissolves in nitrohydrochloric acid. It dissolves partly in caustic alkalies, with separation of platinum, and completely in alkaline sulphides, especially the polysulphides if used in sufficient excess. When sulphuretted hydrogen is transmitted through water holding minutely divided bisulphide of platinum in suspension, the bisulphide, absorbing sulphuretted hydrogen, acquires a light grayish-brown color; the sulphuretted hydrogen thus absorbed, separates again upon exposure to the air. When moist bisulphide of platinum is exposed to the air, it is gradually decomposed, being converted into metallic platinum and sulphuric acid. Ignition in the air reduces bisulphide of platinum to the metallic state.

§ 90.

3. Teroxide of Antimony.

Antimony is weighed as TERSULPHIDE, as ANTIMONIOUS ACID, or more rarely in the METALLIC state.

a. Upon transmitting sulphuretted hydrogen through a solution of terchloride of antimony mixed with tartaric acid, an orange precipitate of amorphous *tersulphide* is obtained, mixed at first with a small portion of basic terchloride of antimony. However, if the fluid is thoroughly saturated with sulphuretted hydrogen, and a gentle heat applied, the terchloride mixed with the precipitate is decomposed, and the pure tersulphide obtained. Tersulphide of antimony is insoluble in water and dilute acids; it dissolves in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen. In precipitating with sulphuretted hydrogen, therefore, antimony solutions should not contain too much free hydrochloric acid, and should be sufficiently diluted. The amorphous tersulphide dissolves readily in dilute potassa, sulphide of ammonium, and sulphide of potassium, sparingly in ammonia, very slightly in carbonate of ammonia, and not at all in bisulphite of potassa. The amorphous sulphide, dried in the desiccator at the ordinary temperature, loses very little weight at 100°; if kept for some time at this latter temperature its weight remains constant. But it still retains a little water, which does not perfectly escape even at 190°, but at 200° the sulphide becomes anhydrous, turning black and crystalline (H. ROSE* and Expt. No. 54). Ignited gently in a stream of carbonic acid, the weight of this anhydrous sulphide remains constant; at a stronger heat a small amount volatilizes. The amorphous sulphide, if long exposed to the action of air, in presence of water, slowly takes up oxygen, so that on treatment with tartaric acid it yields a filtrate containing teroxide.

The pentasulphide of antimony is insoluble in water, also in water containing sulphuretted hydrogen. It dissolves completely in ammonia, especially on warming; traces only dissolve in carbonate of ammonia. On heating the dried pentasulphide in a current of carbonic acid 2 eq. sulphur escape, black crystalline tersulphide remaining.

On treating the ter- or pentasulphide with fuming nitric acid violent oxidation sets in. We obtain first antimonic acid and pulverulent sulphur; on evaporating to dryness antimonic acid and sulphuric acid; and lastly on igniting antimonious acid. The same (antimonious acid) is obtained by igniting the sulphide with 30 to 50 times its amount of oxide of mercury (BUNSEN†). Ignition in a current of hydrogen converts the sulphides of antimony into the metallic state.

COMPOSITION.

Sb	122·00	71·77
S_3	48·00	28·23
	170·00	100·00

b. Antimonious acid is a white powder, which, when heated, acquires transiently a yellow tint; it is infusible; it is fixed, provided reducing gases be excluded. It is almost insoluble in water, and dissolves in hydrochloric acid with very great difficulty. It undergoes no alteration on treatment with sulphide of ammonium. It manifests an acid reaction when placed upon moist litmus-paper.

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* Journ. f. prakt. Chem. 59, 331.

† Annal. d. Chem. u. Pharm. 106, 3.

COMPOSITION.

Sb	122·0	79·22
O_4	32·0	20·78
	154·0	100·00

c. Metallic antimony, produced in the wet way, by precipitation, presents a lustreless black powder. It may be dried at 100° without alteration. It fuses at a moderate red heat. Upon ignition in a current of gas, *e.g.*, hydrogen, it volatilizes, without formation of antimonetted hydrogen. Hydrochloric acid has very little action on it, even when concentrated and boiling. Nitric acid converts it into teroxide of antimony, mixed with more or less antimonious acid, according to the concentration of the nitric acid.

§ 91.

4. Protoxide of Tin; and 5. Binoxide of Tin.

Tin is generally weighed in the form of BINOXIDE; besides the binoxide, we have to examine PROTOSULPHIDE and BISULPHIDE OF TIN.

a. Binoxide of tin.—The hydrate of the binoxide *b* (*hydrated metastannic acid*) is obtained in the form of a white precipitate, by the action of nitric acid upon metallic tin, or by evaporating a solution of tin with nitric acid in excess. This precipitate is insoluble in water and but very slightly in nitric acid and dilute sulphuric acid. By heating with hydrochloric acid, metachloride of tin is formed which is insoluble in hydrochloric acid, but soluble in water after the expulsion of the excess of acid. It reddens litmus, even when thoroughly washed. But if we precipitate solution of bichloride of tin with an alkali, or with sulphate of soda, or nitrate of ammonia, we obtain the hydrate of the binoxide *a*, which dissolves readily in hydrochloric acid. If soda is added in excess to metachloride of tin solution, metastannate of soda is separated, which is insoluble in soda and weak spirit; but if soda is added to ordinary chloride of tin, the precipitate dissolves in excess and does not separate again even on addition of a large quantity of soda (C. F. BARFOED[*]). Upon intense ignition, both hydrates are converted into the anhydrous binoxide of tin. Mere heating to redness is not sufficient to expel all the water (DUMAS[†]).

Binoxide of tin is a straw-colored powder, which under the influence of heat, transiently assumes a different tint, varying from bright yellow to brown. It is insoluble in water and acids, and does not alter the color of litmus-paper. Mixed with chloride of ammonium in excess, and ignited, it volatilizes completely as bichloride. If binoxide of tin is fused with cyanide of potassium, all the tin is obtained in form of metallic globules, which may be completely, and without the least loss of metal, freed from the adhering slag, by extracting with dilute spirit of wine and rapidly decanting the fluid from the tin globules (H. ROSE[‡]).

[*] Zeitschr. f. anal. Chem. 7, 260.

[†] Annal. d. Chem. u. Pharm. 105, 104.

[‡] Journ. f. prakt. Chem. 61, 189.

COMPOSITION.

Sn	59	78·67
O_2	16	21·33
	75	100·00

b. Hydrated protosulphide of tin forms a brown precipitate, insoluble in water, sulphuretted hydrogen water, and dilute acids. In precipitating tin from solutions of the protoxide by means of sulphuretted hydrogen, free hydrochloric acid must not be present in too large amount, and the solution must be diluted sufficiently. Ammonia fails to dissolve it; but it dissolves pretty readily (as bisulphide) in the yellow sulphide of ammonium, and in the yellow sulphide of potassium; it dissolves readily in hot concentrated hydrochloric acid. Heated, with exclusion of air, it loses its water, and is rendered anhydrous; when exposed to the continued action of a gentle heat, with free access of air, it is converted into sulphurous acid, which escapes, and binoxide of tin, which remains.

c. Hydrated bisulphide of tin precipitated by acids from the solution of its alkaline sulphosalts is a light-yellow precipitate. In washing with pure water, it is inclined to yield a turbid filtrate and to stop up the pores of the filter; this annoyance is got over by washing with water containing chloride of sodium, acetate of ammonia, or the like (BUNSEN). On drying, the precipitate assumes a darker tint. It is insoluble in water; it dissolves with difficulty in ammonia, but readily in potassa, alkaline sulphides, and hot concentrated hydrochloric acid. It is insoluble in bisulphite of potassa. In precipitating tin from solutions of the binoxide by sulphuretted hydrogen, the solution should not contain too much free hydrochloric acid, and should be sufficiently diluted. According to C. F. BARFOED* the precipitates thus produced are not pure hydrated bisulphide, but a mixture of this with hydrated stannic or metastannic acid, as the case may be. The precipitate thrown down from ordinary chloride of tin keeps its yellow color even after long standing in the fluid and dissolves completely in excess of soda; that thrown down from the metachloride is first white and becomes gradually yellow, it turns brown on standing in the fluid and dissolves in excess of soda, leaving, however, a considerable residue of metastannate of soda. When heated, with exclusion of air, the sulphide loses its water of hydration, and, at the same time, according to the degree of heat, one-half, or a whole equivalent of sulphur, becoming converted either into sesquisulphide, or into protosulphide of tin; when heated very slowly, with free access of air, it is converted into binoxide of tin, with disengagement of sulphurous acid.

§ 92.

6. ARSENIOUS ACID; and 7. ARSENIC ACID.

ARSENIC is weighed either as ARSENIATE OF LEAD, as TERSULPHIDE, as ARSENIATE OF MAGNESIA AND AMMONIA, as ARSENIATE OF MAGNESIA, as ARSENIATE OF URANIUM, or as BASIC ARSENIATE

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* Zeitschr. f. anal. Chem. 7, 261.

OF SESQUIOXIDE OF IRON ; besides these forms, we have here to examine also ARSENIO-MOLYBDATE OF AMMONIA.

a. Arseniate of lead, in the pure state, is a white powder, which agglutinates when exposed to a gentle red heat, at the same time transitorily acquiring a yellow tint; it fuses when exposed to a higher degree of heat. When strongly ignited, it suffers a slight diminution of weight, losing a small proportion of arsenic acid, which escapes as arsenious acid and oxygen. In analysis we have never occasion to operate upon the pure arseniate of lead, but upon a mixture of it with oxide of lead.

b. Tersulphide of arsenic forms a precipitate of a rich yellow color; it is insoluble in water,* and also in sulphuretted hydrogen water. When boiled with water, or left for several days in contact with that fluid, it undergoes a very trifling decomposition: a trace of arsenious acid dissolves in the water, and a minute proportion of sulphuretted hydrogen is disengaged. This does not in the least interfere, however, with the washing of the precipitate. The precipitate may be dried at 100°, without decomposition; the whole of the water which it contains is expelled at that temperature. When exposed to a stronger heat, it transitorily assumes a brownish-red color, fuses, and finally rises in vapor, without decomposition. It dissolves readily in alkalies, alkaline carbonates, alkaline sulphides, bisulphite of potassa, and nitrohydrochloric acid; but it is scarcely soluble in boiling concentrated hydrochloric acid. Red fuming nitric acid converts it into arsenic acid and sulphuric acid. It is insoluble in sulphide of carbon.

COMPOSITION.

As	75	60·98
S_3	48	39·02
	123	100·00

c. Arseniate of magnesia and ammonia forms a white, somewhat transparent, finely crystalline precipitate, which when dried in a desiccator has the formula $2MgO,NH_4O,AsO_5 + 12$ aq. At 100°, it loses 11 eq. water; the formula of the precipitate dried at that temperature is accordingly $2MgO,NH_4O,AsO_5 +$ aq. At a higher temperature, say 105°—110°, more water escapes, and at 130° this loss is considerable (PULLER†). Upon ignition it loses its water and ammonia, and changes to $2MgO,AsO_5$. On rapid ignition the escaping ammonia has a reducing action on the arsenic acid, and a notable loss is occasioned (H. ROSE); by raising the heat very gradually reduction may be avoided (H. ROSE, WITTSTEIN,‡ PULLER), or by passing a current of dry oxygen during the ignition. Arseniate of magnesia and ammonia dissolves very sparingly in water, one part of the salt dried at 100°, requiring 2656, one part of the anhydrous salt, 2788 parts of water of 15°. It is far less soluble in ammoniated water, one part of the salt dried at 100° requiring 15038, one part of the anhydrous salt, 15786 parts of a mixture of one part of solution of ammonia (·96 sp. gr.), and 3 parts of water at 15°. In water containing chloride of ammonium, it is much more readily soluble, one part of the anhydrous salt requiring 886 parts of a solution of one part of chloride of ammonium in 7 parts of water. Presence of ammonia diminishes the solvent capacity of the chloride of ammonium; one part of the anhydrous salt requires 3014 parts of a mixture of 60 parts of water, 10 of solution of ammonia (·96 sp. gr.) and one of chloride of ammonium.* A solution of chloride of ammonium, ammonia and sulphate of magnesia dissolves much less of the salt than ammoniated water; thus, PULLER (loc. cit.) found that one part of the anhydrous salt dissolved in 32827 parts of a fluid containing $\frac{1}{20}$ of magnesia mixture (p. 98). Excess of alkaline arseniate still more diminishes the solubility of the salt in water containing ammonia and chloride of ammonium (PULLER).

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* In some experiments which I had occasion to make, in the course of an analysis of the springs of Weilbach (Chemische Untersuchung der wichtigsten Nassauischen Mineralwasser von Dr. Fresenius, V. Schwefelquelle zu Weilbach. Wiesbaden, Kreidel und Niedner. 1856), I found that one part of AsS_3 dissolves in about 1 million parts of water.

† Zeitschr. f. anal. Chem. 10, 62.

‡ *Ib.* 2, 19.

COMPOSITION OF THE ARSENIATE OF MAGNESIA AND AMMONIA DRIED AT 100°.

$2\,MgO$	40·00	21·05
NH_4O	26·04	13·68
AsO_5	115·00	60·53
HO	9·00	4·74
	190·04	100·00

d. Arseniate of magnesia, obtained by careful ignition of the preceding salt, is white, infusible by ignition in a porcelain crucible even over the blowpipe, but agglutinating at a still higher temperature, and finally fusing. After ignition in a porcelain crucible it dissolves readily in hydrochloric acid, ammonia precipitates the arseniate of ammonia and magnesia from the solution in a crystalline form.

COMPOSITION.

$2MgO$	40	25·81
AsO_5	115	74·19
	155	100·00

e. Arseniate of uranium.—If a solution of arsenic acid is mixed with potash in slight excess, then with acetic acid to strongly acid reaction, and finally with acetate of uranium, the whole of the arsenic is thrown down as $2Ur_2O_3,HO,AsO_5 + 8$ aq. In the presence of salts of ammonia the precipitate also contains the whole of the arsenic, and consists of $2Ur_2O_3,NH_4O,AsO_5 +$ aq. Both precipitates are pale yellowish-green, slimy, insoluble in water, acetic acid and saline solutions, such as chloride of ammonium, soluble in mineral acids. Boiling favors the separation of the precipitate, addition of a few drops of chloroform will help it to settle, the washing is to be effected by boiling up and decanting. Both precipitates give $2Ur_2O_3,AsO_5$ on ignition. The latter is a light yellow residue; if it has turned greenish from the action of reducing gases, it may be restored to its proper color by moistening with nitric acid and re-igniting. On igniting the arseniate of ammonia and magnesia, the ammonia must first be expelled by cautious heating, or a current of oxygen must be passed during the ignition, otherwise the arsenic acid will be partially reduced, and arsenic will be lost (PULLER*).

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* Zeitschr. f. anal. Chem. 8, 206. PULLER obtained almost the same numbers (*Ib.* 10, 53).

COMPOSITION.

$2Ur_2O_3$	285·6	71·29
AsO_5	115·0	28·71
	400·6	100·00

f. Arseniate of sesquioxide of iron.—The white slimy precipitate, produced by the action of ordinary arseniate of soda upon solution of sesquichloride of iron, has the composition $2Fe_2O_3,3HO,3AsO_5 + 9$ aq. It dissolves in mineral acids, but is only soluble in arsenic acid when the solution is cold and very concentrated. By diluting or heating such a solution, a precipitate of arseniate of iron falls; in the latter case, the precipitate does not redissolve on cooling (LUNGE†). It dissolves in solution of ammonia with a yellow color. Besides this compound, there exists still several others, with larger proportions of sesquioxide of iron; thus we have Fe_2O_3,AsO_5, which falls down + 5 aq. upon the precipitation of arsenic acid with acetate of sesquioxide of iron (KOTSCHOUBEY); $2Fe_2O_3,AsO_5$, which is obtained + 12 aq., when basic arseniate of protoxide of iron is oxidized with nitric acid, and ammonia added;—$16Fe_2O_3,AsO_5$, which forms + 24 aq. upon boiling the less basic compounds with solution of potassa in excess (BERZELIUS). The two latter compounds are not soluble in ammonia; the last is quite like hydrated sesquioxide of iron. In BERTHIER's method of estimating arsenic acid, we obtain mixtures of these different salts. They are the better adapted for the purpose, the more basic they are; being the more insoluble in ammonia, and at the same time more easily washed. Upon ignition the water alone is expelled, provided the heat be very gradually increased. But if the salt is suddenly exposed to a strong heat, before the adhering ammonia has escaped, part of the arsenic acid is thereby reduced to arsenious acid (H. ROSE).

g. Arsenio-molybdate of ammonia.—If a fluid containing arsenic acid is mixed with excess of the nitric acid solution of molybdate of ammonia, the fluid remains clear in the cold, but on heating a yellow precipitate of arsenio-molybdate of ammonia separates. This precipitate comports itself with solvents like the analogous compound of phosphoric acid; it is, like the latter, insoluble in water, nitric acid, dilute sulphuric acid and salts, provided an excess of solution of molybdate of ammonia, mixed with acid in moderate excess, be present. Hydrochloric acid or metallic chlorides, when present in large quantity, interfere with the thoroughness of the precipitation. SELIGSOHN‡ found it to be composed of 87·666 per cent. of molybdic acid, 6·308 arsenic acid, 4·258 ammonia, and 1·768 water.

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* Zeitschr. f. anal. Chem 10, 72.

† *Ib.* 6, 185.

‡ Journ. f. prakt. Chem. 67, 481.

B.—FORMS IN WHICH THE ACIDS ARE WEIGHED OR PRECIPITATED.

ACIDS OF THE FIRST GROUP.

§ 93.

1. ARSENIOUS ACID and ARSENIC ACID.—See § 92.

2. CHROMIC ACID.

Chromic acid is weighed either as SESQUIOXIDE, or as CHROMATE OF LEAD, or CHROMATE OF BARYTA. We have also to consider the SUBCHROMATE OF MERCURY.

a. Sesquioxide of chromium.—See § 76.

b. Chromate of lead obtained by precipitation forms a bright yellow precipitate, insoluble in water and acetic acid, barely soluble in dilute nitric acid, readily in solution of potassa. When chromate of lead is boiled with concentrated hydrochloric acid, it is readily decomposed, chloride of lead and sesquichloride of chromium being formed. Addition of alcohol tends to promote this decomposition. Chromate of lead is unalterable in the air; it dries thoroughly at 100°. Under the influence of heat it transitorily acquires a reddish-brown tint; it fuses at a red heat; when heated beyond its point of fusion, it loses oxygen, and is transformed into a mixture of sesquioxide of chromium and basic chromate of lead. Heated in contact with organic substances, it readily yields oxygen to the latter.

COMPOSITION.

PbO	111·50	68·94
CrO_3	50·24	31·06
	161·74	100·00

c. Chromate of baryta is obtained as a light yellow precipitate on mixing a solution of an alkaline chromate with chloride of barium. It dissolves in hydrochloric and in nitric acid, but not in acetic acid. On washing with pure water, the latter begins to dissolve it slightly, as soon as all soluble salts are removed, to such an extent that the washings run off yellow. The precipitate is insoluble in saline solutions. Hence it is best to use a solution of acetate of ammonia for washing (PEARSON and RICHARDS*). It is not decomposed by moderate ignition.

COMPOSITION.

BaO	76·50	60·36
CrO_3	50·24	39·64
	126·74	100·00

d. Chromate of suboxide of mercury obtained by adding nitrate of suboxide of mercury to an alkaline chromate is a brilliant red precipitate, which turns black by the action of light. It dissolves very slightly in cold water, more in boiling water, being partially converted into a salt of the oxide; it dissolves slightly in dilute nitric acid.

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* Zeitschr. f. anal. Chem. 9, 108.

For washing, it is best to use a dilute solution of nitrate of suboxide of mercury containing but little free acid; in this solution it is insoluble (H. Rose*).

3. Sulphuric Acid.

Sulphuric acid is determined best in the form of SULPHATE OF BARYTA, for the properties of which see § 71.

4. Phosphoric Acid.

The principal forms into which phosphoric acid is converted are as follows:—PHOSPHATE OF LEAD, PYROPHOSPHATE OF MAGNESIA, BASIC PHOSPHATE OF MAGNESIA ($3MgO,PO_5$), BASIC PHOSPHATE OF SESQUIOXIDE OF IRON, PHOSPHATE OF SESQUIOXIDE OF URANIUM, PHOSPHATE OF BINOXIDE OF TIN, and PHOSPHATE OF SILVER. Besides these compounds, we have to examine PHOSPHATE OF SUBOXIDE OF MERCURY, and PHOSPHO-MOLYBDATE OF AMMONIA.

a. The *phosphate of lead* obtained in the course of analysis is rarely pure, but is generally mixed with free oxide of lead. In this mixture we have accordingly the basic phosphate of lead ($3PbO,PO_5$); in the pure state, this presents the appearance of a white powder; it is insoluble in water, acetic acid, and ammonia; it dissolves readily in nitric acid. When heated it fuses without decomposition.

b. Pyrophosphate of magnesia.—See § 74.

c. Basic phosphate of magnesia ($3MgO,PO_5$).—A mixture of this compound with excess of magnesia is produced by mixing a solution of an alkaline phosphate, containing chloride of ammonium, with magnesia, evaporating, heating until the chloride of ammonium is expelled, and finally treating with water. It is practically insoluble in water and in solutions of salts of the alkalies (Fr. Schulze†).

d. Basic phosphate of sesquioxide of iron.—If a solution of phosphoric acid or of phosphate of lime in acetic acid is carefully precipitated with a solution of acetate of sesquioxide of iron, or with a mixture of iron-alum and acetate of soda, so that the iron salt may just predominate, the precipitate always contains 1 eq. PO_5 to 1 eq. Fe_2O_3 (Rawsky, Wittstein, E. Davy‡); if, on the other hand, the acetate of iron is in larger excess, the precipitate contains more base. Wittstein obtained, by using considerable excess of acetate of iron, a precipitate of the formula $4\ Fe_2O_3,3PO_5$. Precipitates, obtained with a small excess of the precipitant, possess a composition varying between the above-mentioned limits. Rammelsberg obtained $Fe_2O_3,PO_5(+4\ aq.)$, and Wittstein subsequently, the same compound (with 8 aq. instead of 4), upon mixing sulphate of sesquioxide of iron with phosphate of soda in excess; with an insufficient quantity of the phosphate of soda, the latter chemist obtained a more yellowish precipitate, which had the formula $3(Fe_2O_3,PO_5 + 8\ aq.) + (Fe_2O_3,3HO)$. If an acid fluid containing a *considerable* excess of phosphoric acid is mixed with a small quantity of solution of sesquioxide of iron, and an alkaline acetate added, a precipitate of the formula, Fe_2O_3,PO_5, + water, is invariably obtained, which, accordingly, leaves upon ignition Fe_2O_3,PO_5 (Wittstein). Fresh experiments that I have made upon this subject have convinced me of the perfect correctness of this statement. **Mohr** obtained the same results.* The precipitate is insoluble in a fluid containing salts, but when washing, as soon as the soluble salts are nearly removed, the precipitate begins to dissolve. The filtrate has an acid reaction, and contains sesquioxide of iron and phosphoric acid. The precipitate, under these circumstances, alters in composition, and this explains why different results were obtained in the analysis of precipitates which had been washing for different lengths of time (Fr. Mohr).

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* Pogg. Ann. 53, 124.

† Journ. f. prakt. Chem. 63, 440.

‡ Phil. Mag. 19, 181.

COMPOSITION.

PO_5	71	47·02
Fe_2O_3	80	52·98
	151	100·00

If we dissolve phosphate of sesquioxide of iron in hydrochloric acid, supersaturate the solution with ammonia, and apply heat, we obtain more basic salts, viz., $3Fe_2O_3,2PO_5$ (Rammelsberg); $2Fe_2O_3,PO_5$ (Wittstein—after long washing). In Wittstein's experiment, the wash-water contained phosphoric acid. The white phosphate of sesquioxide of iron does not dissolve in acetic acid, but it dissolves in a solution of acetate of sesquioxide of iron. Upon boiling the latter solution (of phosphate of sesquioxide of iron in acetate of sesquioxide of iron), the whole of the phosphoric acid precipitates, with the basic acetate of sesquioxide of iron, as hyperbasic phosphate of sesquioxide of iron. Similar extremely basic combinations are invariably obtained (often mixed with free hydrated sesquioxide of iron), upon precipitating with ammonia or carbonate of baryta a solution containing phosphoric acid and an excess of sesquioxide of iron. The precipitate obtained by carbonate of baryta, can be conveniently filtered off and washed, the filtrate is perfectly free from either iron or phosphoric acid; on the contrary, the precipitate obtained by ammonia, especially if the latter were much in excess, is slimy, and therefore difficult to wash, and the filtrate always contains small traces of both iron and phosphoric acid.

e. Phosphate of sesquioxide of uranium.—If the hot aqueous solution of a phosphate soluble in water or acetic acid is mixed, in presence of free acetic acid, with acetate of sesquioxide of uranium, a precipitate of phosphate of sesquioxide of uranium is immediately formed. If the fluid contains much ammoniacal salt, the precipitate contains also ammonia. The same precipitate forms also if alumina or sesquioxide of iron is present; but in that case it is always mixed with more or less phosphate of sesquioxide of iron or phosphate of alumina. Presence of potassa- or soda-salts, on the contrary, or of salts of the alkaline earths, has no influence on the composition of the precipitate. Phosphate of sesquioxide of uranium and ammonia ($2Ur_2O_3,NH_4O,PO_5 + xHO$) is a somewhat gelatinous, whitish-yellow precipitate, with a tinge of green. The best way of washing it, at least so far as the principal part of the operation is concerned, is by boiling with water and decanting. If, after having allowed the fluid in which the precipitate is suspended to cool a little, a few drops of chloroform are added, and the mixture is shaken or boiled up, the precipitate subsides much more readily than without this addition. The precipitate is insoluble in water, slightly soluble in acetic acid, readily soluble in mineral acids; acetate of ammonia, added in sufficient excess, completely reprecipitates it from this solution, upon application of heat. Upon igniting the precipitate, no matter whether containing ammonia or not, phosphate of sesquioxide of uranium of the formula $2Ur_2O_3,PO_5$ is produced. This has the color of the yolk of an egg. If the precipitate is ignited in presence of charcoal or of some reducing gas, partial reduction to phosphate of protoxide of uranium ensues, owing to which the ignited mass acquires a greenish tint; however, upon warming the residue with some nitric acid, it is readily reconverted into the yellow salt. Phosphate of sesquioxide of uranium is not hygroscopic, and may therefore be ignited and weighed in an open platinum dish (A. Arendt and W. Knop*).

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* Zeitschr. f. anal. Chem. 2, 250.

COMPOSITION.

$2Ur_2O_3$	285·6	80·09
PO_5	71·0	19·91
	356·6	100·00†

f. Phosphate of binoxide of tin is never obtained in the pure state in the analytical process, but contains always an admixture of hydrated metastannic acid, which, upon ignition, changes to metastannic acid. It has, generally speaking, the same properties as hydrated metastannic acid, and is more particularly, like the latter, very sparingly soluble in nitric acid. Upon heating with concentrated solution of potassa, phosphate and metastannate of potassa are formed.

g. Tribasic phosphate of silver is a yellow powder, insoluble in water, readily soluble in nitric acid and ammonia. In ammoniacal salts, it is difficultly soluble. It is unalterable in the air. Upon ignition, it acquires transiently a reddish-brown color; at an intense red heat, it fuses without decomposition.

COMPOSITION.

$3AgO$	347·79	83·05
PO_5	71·00	16·95
	418·79	100·00

h. Phosphate of suboxide of mercury.—This compound is obtained in the separation of phosphoric acid from many bases, after H. Rose's method. It presents a white crystalline mass, or a white powder. It is insoluble in water, but dissolves in nitric acid. The action of a red heat converts it into fused phosphate of oxide of mercury, with evolution of vapor of mercury. Upon fusion with alkaline carbonates, alkaline phosphates are produced, while mercury, oxygen, and carbonic acid escape.

i. Phospho-molybdate of ammonia.—This compound also serves to effect the separation of phosphoric acid from other bodies; it is of the utmost importance in this respect. It forms a bright yellow, readily subsiding precipitate. Dried at 100°, it has, according to SELIGSOHN, the following (average) composition:—

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* Chemisches Centralblatt, 1856, 769, 803; and 1857, 177.

† The equivalent of uranium is here taken as 59·4, according to Ebelmen. If we take it according to Péligot, as 60, the ignited phosphate would contain 80·22 Ur_2O_3, and 19·78 phosphoric acid. W. Knop and Arendt found in four experiments 20·13, 20·06, 20·04, and 20·04 respectively (in another 20·77). It will be seen that these numbers agree better with the composition as reckoned from Ebelmen's than from Péligot's equivalent.

Molybdic acid	90·744
Phosphoric acid	3·142
Oxide of ammonium	3·570
Water	2·544
	100·000*

In the pure state, it dissolves but sparingly in cold water (1 in 10000—EGGERTZ); but it is soluble in hot water. It is readily soluble even in the cold, in caustic alkalies, alkaline carbonates and phosphates, chloride of ammonium, and oxalate of ammonia. It dissolves sparingly in sulphate of ammonia, nitrate of potassa, and chloride of potassium; and very sparingly in nitrate of ammonia.

It is soluble in sulphate of potassa and sulphate of soda, chloride of sodium and chloride of magnesium, and sulphuric, hydrochloric and nitric acids (concentrated and dilute). Water, containing 1 per cent. of common nitric acid dissolves $\frac{1}{6600}$ (EGGERTZ). Application of heat does not check the solvent action of these substances. Presence of molybdate of ammonia totally changes its deportment with acid fluids. Dilute nitric or sulphuric acid containing molybdate of ammonia does not dissolve it; but much hydrochloric acid, even in the presence of molybdate of ammonia, has a solvent action, and this acid consequently interferes with the complete precipitation of phosphoric acid by nitric acid solution of molybdate of ammonia. The solution of the phospho-molybdate of ammonia in acids is probably attended, in all cases, with decomposition and separation of the molybdic acid, which cannot take place in the presence of molybdate of ammonia (J. CRAW†). Tartaric acid and similar organic substances entirely prevent the precipitation of the phospho-molybdate of ammonia (EGGERTZ). In the presence of an iodide instead of a yellow precipitate, a green precipitate or a green fluid is formed, resulting from the reducing action of the hydriodic acid on the *molybdic acid* (*J. W. BILL*‡). Other substances which reduce molybdic acid have of course a similar action.

5. BORACIC ACID.

BOROFLUORIDE OF POTASSIUM is the best form to convert boracic acid into for the purpose of the direct estimation of the acid. This compound is produced by mixing the solution of an alkaline borate, in presence of a sufficient quantity of potassa, with hydrofluoric acid in excess, in a silver or platinum dish, and evaporating to dryness. The gelatinous precipitate which forms in the cold, dissolves upon application of heat, and separates from the solution subsequently, upon evaporation, in small, hard, transparent crystals. The compound has the formula KF,BF_3. It is soluble in water and also in dilute spirit of wine; but strong alcohol fails to dissolve it; it is insoluble also in concentrated solution of acetate of potassa. It may be dried at 100°, without decomposition (AUG. STROMEYER*).

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* From the varying results of different analysts it is plain that the precipitate, prepared under apparently the same circumstances, has not always exactly the same composition SONNENSCHEIN (Journ. f prakt. Chem. 53, 342) found in the precipitate dried at 120°, 2·93—3·12 $^0/_0$ PO_5; LIPOWITZ (Pogg. Annal. 109, 135), in the precipitate dried at from 20 to 30°, 3·607 $^0/_0$ PO_5; EGGERTZ (Journ. f. prakt. Chem. 79, 496), 3·7 to 3·8 $^0/_0$.

† Chem. Gaz. 1852, 216.

‡ Sillim. Journ., July, 1858.

COMPOSITION.

K	39·13	31·02
B	11·00	8·72
F_4	76·00	60·26
	126·13	100·00

6. OXALIC ACID.

When oxalic acid is to be directly determined it is usually precipitated in the form of OXALATE OF LIME; and its weight is inferred from the CARBONATE OF LIME or LIME produced from the oxalate by ignition. For the properties of these bodies see § 73.

7. HYDROFLUORIC ACID.

The *direct* estimation of hydrofluoric acid is usually effected by weighing the acid in the form of FLUORIDE OF CALCIUM.

Fluoride of calcium forms a gelatinous precipitate, which it is found difficult to wash. If digested with ammonia, previous to filtration, it is rendered denser and less gelatinous. It is not altogether insoluble in water; aqueous solutions of the alkalies fail to decompose it. It is very slightly soluble in dilute, but more readily in concentrated hydrochloric acid. When acted upon by sulphuric acid, it is decomposed, and sulphate of lime and hydrofluoric acid are formed. Fluoride of calcium is unalterable in the air, and at a red heat. Exposed to a very intense heat, it fuses. Upon intense ignition in moist air, it is slowly and partially decomposed into lime and hydrofluoric acid. Mixed with chloride of ammonium, and exposed to a red heat, fluoride of calcium suffers a continual loss of weight; but the decomposition is incomplete.

COMPOSITION.

Ca	20	51·28
F	19	48·72
	39	100·00

We often determine fluorine, more particularly in presence of silicic acid, by converting it into *fluoride of silicon* ($Si\ F_2$). This is a colorless gas, fuming in the air, with suffocating odor, of sp. gr. 3·574, which decomposes when mixed with water forming silicic acid and hydrofluosilicic acid thus: $3\ Si\ F_2 + 2HO = 2\ (Si\ F_2,\ HF) + Si\ O_2$.

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* Annal. d. Chem. u. Pharm. 100, 82.

8. CARBONIC ACID.

The *direct* estimation of carbonic acid—which, however, is only rarely resorted to—is usually effected by weighing the acid in the form of CARBONATE OF LIME. For the properties of the latter substance, see § 73.

9. SILICIC ACID.

When silicic acid is separated by acids from aqueous solutions of alkaline silicates, it is at first perfectly soluble in water. It becomes insoluble or rather difficultly soluble when it coagulates. Coagulation is a permanent change and is furthered by concentration and by elevation of temperature. Silicic acid solution of 10 or 12 per cent. coagulates at the ordinary temperature in a few hours, and immediately if heated. A solution of 5 per cent. may be preserved without coagulating for five or six days, one of 2 per cent. for two or three months, and one of 1 per cent. for several years, and solutions containing $\frac{1}{10}$ per cent. or less are not appreciably altered by time. Solid matter in powder such as graphite, hastens coagulation, alkaline salts induce it rapidly. Aqueous solutions of silicic acid may on the contrary be mixed with hydrochloric acid, nitric acid, acetic acid, tartaric acid and alcohol without coagulating. The gelatinous silicic acid produced by coagulation may contain more or less water, and it appears to be the more difficultly soluble in water, the less water it contains; thus a jelly of 1 per cent. of silicic acid gives a solution with cold water containing 1 part of silicic acid in about 5000 parts, a jelly of 5 per cent. gives a solution containing 1 part of silicic acid in about 10000 parts of water. A jelly containing less water is still less soluble, and when the jelly is dried up to a gummy mass it is barely soluble at all; this is also the case with the pulverulent hydrate of silicic acid obtained in the analysis of silicates by drying a jelly containing much salts at 100° (GRAHAM*). The hydrate dried at 100° dissolves but very slightly in acids (with the exception of hydrofluoric acid), it dissolves, however, in solutions of pure and carbonated fixed alkalies, especially on heating. Aqueous ammonia dissolves the jelly in tolerable quantity and the dry hydrate in very notable quantity (PRIBRAM†). Regarding the amount of water in the hydrate dried at given temperatures chemists do not agree.‡

On ignition all the hydrates pass into the anhydrous acid. As the vapor escapes small particles of the extremely fine powder are liable to whirl up. This may be avoided by moistening the hydrate in the crucible with water, evaporating to dryness on a water bath, and then applying at first a slight and then a gradually increased heat.

The silicic acid obtained by igniting the hydrate appears in the amorphous condition, with a sp. gr. of 2·2 to 2·3. It forms a white powder insoluble in water, and acids (hydrofluoric excepted), soluble in solutions of the fixed alkalies and their carbonates, especially in the heat. Hydrofluoric acid readily dissolves amorphous silicic acid; the solution leaves no residue on evaporation in platinum, if the silica was pure. The amorphous silica, when heated with fluoride of ammonium in a platinum crucible, readily volatilizes. The ignited amorphous silica, exposed to the air, eagerly absorbs water, which it will not give up at from 100 to 150° (H. ROSE). The lower the heat during ignition the more hygroscopic is the residue (SOUCHAY*). Silica fuses at the strongest heat; the mass obtained being vitreous and amorphous. Amorphous silica ignited with chloride of ammonium, at first loses weight, and then, when the ignition has rendered it denser, the weight remains constant.

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* Pogg. Annal. 123, 529. † Zeitschr. f. anal Chem. 6, 119.

‡ DOVERI (Annal. de Chim. et de Phys. 21, 40 ; Annal. d. Chem. u. Pharm. 64, 256) found in the air-dried hydrate 16·9 to 17·8 % water ; J. FUCHS (Annal. d. Chem. u. Pharm. 82, 118 to 123), 9·1 to 9·6 : G. LIPPERT, 9·28 to 9·95. DOVERI found in the hydrate dried at 100°, 8·3 to 9·4 ; J. FUCHS, 6·63 to 6·96 ; G. LIPPERT, 4·97 to 5·52. H. ROSE (Pogg. Annal. 108, 1 ; Journ. fur prakt. Chem. 81, 227) found in the hydrate obtained by digesting stilbite with concentrated hydrochloric acid, and dried at 150°, 4·85 % water.

The amorphous silica must be distinguished from the crystallized or crystalline variety, which occurs as rock crystal, quartz, sand, &c. This has a sp. gr. of 2·6 (SCHAFFGOTSCH), and is far more difficultly, and in far less amount, dissolved by potash solution or solution of fixed alkaline carbonates; it is also more slowly attacked by hydrofluoric acid, or fluoride of ammonium. Crystallized silica is not hygroscopic, whether strongly or gently ignited (SOUCHAY). Vegetable colors are not changed either by silicic acid or its hydrates.

COMPOSITION.

Si	14·00	46·67
O_2	16·00	53·33
	30·00	100·00

ACIDS OF THE SECOND GROUP.

§ 94.

1. HYDROCHLORIC ACID.

Hydrochloric acid is almost invariably weighed in the form of CHLORIDE OF SILVER—for the properties of which see § 82.

2. HYDROBROMIC ACID.

Hydrobromic acid is always weighed in the form of BROMIDE OF SILVER.

Bromide of silver, prepared in the wet way, forms a yellowish-white precipitate. It is wholly insoluble in water and in nitric acid, tolerably soluble in ammonia, readily soluble in hyposulphite of soda and cyanide of potassium. Concentrated solutions of the chlorides and bromides of potassium, sodium, and ammonium dissolve it to a very perceptible amount, while in very dilute solutions of these salts it is entirely insoluble. Traces only dissolve in nitrates of the alkalies. It dissolves abundantly in a concentrated warm solution of nitrate of mercury. On digestion with excess of iodide of potassium solution it is completely converted into iodide of silver (FIELD). On ignition in a current of chlorine the bromide of silver is transformed into the chloride; on ignition in a current of hydrogen it is converted into metallic silver. Exposed to the light it gradually turns gray, and finally black. Under the influence of heat, it fuses to a reddish liquid, which, upon cooling, solidifies to a yellow, horn-like mass. Brought into contact with zinc and water, it is decomposed: a spongy mass of metallic silver forms, and the solution contains bromide of zinc.

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* Zeitschr. f. anal. Chem. 8, 423.

COMPOSITION.

Ag	107·93	57·45
Br	79·95	42·55
	187·88	100·00

3. Hydriodic Acid.

Hydriodic acid is usually determined in the form of IODIDE OF SILVER, and occasionally also in that of PROTIODIDE OF PALLADIUM.

a. Iodide of silver, produced in the wet way, forms a light-yellow precipitate, insoluble in water, and in dilute nitric acid, and very slightly soluble in ammonia. One part dissolves, according to **Wallace** and **Lamont**[*] in 2493 parts of aqueous ammonia sp. gr. ·89, according to **Martini**, in 2510 parts of ·96 sp. gr. It is copiously taken up by concentrated solution of iodide of potassium, but it is insoluble in very dilute; it dissolves readily in hyposulphite of soda and in cyanide of potassium; traces only are dissolved by alkaline nitrates. In concentrated warm solution of nitrate of mercury it is copiously soluble. Hot concentrated nitric and sulphuric acids convert it, but with some difficulty, into nitrate and sulphate of silver respectively, with expulsion of the iodine. Iodide of silver acquires a black color when exposed to the light. When heated, it fuses without decomposition to a reddish fluid, which, upon cooling, solidifies to a yellow mass, that may be cut with a knife. Under the influence of excess of chlorine in the heat it is completely converted into chloride of silver; ignition in hydrogen reduces it but incompletely to the metallic state. When brought into contact with zinc and water, it is decomposed but incompletely: iodide of zinc is formed, and metallic silver separates.

COMPOSITION.

Ag	107·93	45·97
I	126·85	54·03
	234·78	100·00

b. Protiodide of palladium, produced by mixing an alkaline iodide with protochloride of palladium, is a deep brownish-black, flocculent precipitate, insoluble in water, and in dilute hydrochloric acid, but slightly soluble in saline solutions (chloride of sodium, chloride of magnesium, chloride of calcium, &c.). It is unalterable in the air. Dried simply in the air it retains one equivalent of water = 5·05 per cent. Dried long *in vacuo*, or at a rather high temperature (70° to 80°), it yields the whole of this water, without the least loss of iodine. Dried at 100°, it loses a trace of iodine; at from 300° to 400°, the whole of the iodine is expelled. It may be washed with hot water, without loss of iodine.

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[*] Chem. Gaz. 1859, 137.

COMPOSITION.

Pd	53·29	29·58
I	126·85	70·42
	180·14	100·00

4. Hydrocyanic Acid.

Hydrocyanic acid, if determined gravimetrically and directly, is always converted into CYANIDE OF SILVER—for the properties of which compound see § 82.

5. Hydrosulphuric Acid.

The forms into which sulphuretted hydrogen, or the sulphur in metallic sulphides, is converted for the purpose of being weighed, are TERSULPHIDE OF ARSENIC, SULPHIDE OF SILVER, SULPHIDE OF COPPER, and SULPHATE OF BARYTA.

For the properties of the sulphides named, see §§ 82, 85, 92; for those of sulphate of baryta, see § 71.

ACIDS OF THE THIRD GROUP.

§ 95.

1. Nitric Acid; and 2. Chloric Acid.

These two acids are never estimated in a direct way—that is to say, in compounds containing them, but always in an indirect way; generally volumetrically.

SECTION IV.

THE DETERMINATION (OR ESTIMATION) OF BODIES.

§ 96.

In the preceding Section we have examined the composition and properties of the various forms and combinations in which bodies are separated from others, or in which they are weighed. We have now to consider the special means and methods of converting the several bodies into such forms and combinations.

For the sake of greater clearness and simplicity, we shall, in the present Section, confine our attention to the various methods applied to effect the *estimation of single bodies*, deferring to the next Section the consideration of the means adopted for the estimation of mixed bodies, or the separation of bodies from one another.

We have to deal here exclusively with bodies in the free state, or with compounds consisting of one base and one acid, or of one metal and one metalloid.

As in the "Qualitative Analysis," the acids of arsenic will be treated of among the bases, on account of their behavior to sulphuretted hydrogen, and those elements which form acids with hydrogen will be considered in conjunction with their respective hydrogen acids.

In the quantitative analysis of a body we have to study first, the most appropriate method of dissolving it; and secondly, the modes of determining it.

With regard to the latter point, we have to turn our attention, first, to the performance; and secondly, to the accuracy of the methods.

It happens very rarely in quantitative analyses that the amount of a substance, as determined by the analytical process, corresponds exactly with the amount theoretically calculated or actually present; and if it does happen, it is merely by chance.

It is of importance to inquire what is the reason of this fact, and what are the limits of inaccuracy in the several methods.

The cause of this almost invariably occurring discrepancy between the quantity present and that actually found, is to be ascribed either exclusively to the execution, or it lies partly in the method itself.

The execution of the analytical processes and operations can never be absolutely accurate, even though the greatest care and attention be bestowed on the most trifling minutiæ. To account for this, we need only bear in mind that our weights and measures are never absolutely correct, nor our balances absolutely accurate, nor our reagents absolutely pure; and, moreover, that we do not weigh in vacuo; and that, even if we deduce the weight in vacuo from the weight we actually obtain by weighing in the air, the very volumes on which the calculation is based are but approximately known;—that the hygroscopic state of the air is liable to vary between the weighing of the empty crucible and of the crucible + the substance;—that we know the weight of a filter ash only approximately;—that we can never succeed in completely keeping off dust, &c.

With regard to the methods, many of them are not entirely free from certain unavoidable sources of error;—precipitates are not absolutely insoluble; compounds which require ignition are not absolutely fixed; others, which require drying, have a slight tendency to volatilize; the final reaction in volumetric analyses is usually produced only by a small excess of the standard fluid, which is occasionally liable to vary with the degree of dilution, the temperature, &c.

Strictly speaking, no method can be pronounced quite free from defect; it should be borne in mind, for example, that even sulphate of baryta is not absolutely insoluble in water. Whenever we describe any method as free from sources of error, we mean, that no causes of considerable inaccuracy are inherent in it.

We have, therefore, in our analytical processes, invariably to contend against certain sources of inaccuracy which it is impossible to overcome entirely, even though our operations be conducted with the most scrupulous care and with the utmost attention to established rules. It will be readily understood that several defects and sources of error may, in some cases, combine to vitiate the results; whereas, in other cases, they may compensate one another, and thus enable us to attain a higher degree of accuracy. The comparative accuracy of the results attainable by an analytical method oscillates between two points—these points are called the limits of error. In the case of methods free from sources of error, these limits will closely approach each other; thus, for instance, in the estimations of chlorine, with great care one will always be able to obtain between 99·9 and 100·1 for the 100 parts of chlorine actually present.

Less perfect methods will, of course, exhibit far greater discrepancies; thus, in the estimation of boracic acid as borofluoride of potassium, the most attentive and skilful operator may not be able to obtain more than 99·0 (and even less) for the 100 parts of boracic acid actually present. I may here incidentally state that the numbers occasionally given in this manner, in the course of the present work, to denote the degree of accuracy of certain methods, refer invariably to the substance estimated (chlorine, nitrogen, baryta, for instance), and not to the combination in which that substance may be weighed (chloride of silver, bichloride of platinum and chloride of ammonium, sulphate of baryta, for instance); otherwise the accuracy of various methods would not be comparable.

The occasional attainment of results exactly corresponding with the numbers calculated does not always justify the assumption, on the part of the student, that his operations, to have led to such a result, must have been conducted with the utmost precision and accuracy. It may sometimes happen, in the course of the analytical process, that one error serves to compensate another; thus, for instance, the analyst may, at the commencement of his operations, spill a minute portion of the substance to be analysed; whilst, at a later stage of the process, he may recover the loss by an imperfect washing of the precipitate.

As not the least effective means of guarding against error and inaccuracies in *gravimetric analyses*, I would most strongly recommend the analyst, *after weighing a precipitate, &c., to compare its properties (color, solubility, reaction, &c.) with those which it should possess,* and which have been amply described in the preceding Section.

In my own laboratory, I insist upon all substances that are weighed in the course of an analysis being kept between watch-glasses, until the whole affair is concluded. This affords always a chance of testing them once more for some impurity, the presence of which may become suspected in the after-course of the process.

I. ESTIMATION OF BASES IN COMPOUNDS CONTAINING ONLY ONE BASE AND ONE ACID, OR ONE METAL AND ONE METALLOID.

FIRST GROUP.

POTASSA—SODA—AMMONIA—(LITHIA).

§ 97.

1. POTASSA.

a. Solution.

Potassa and its salts with those inorganic acids which we have to consider here are dissolved in water, in which menstruum they dissolve readily, or at all events, pretty readily.

Potassa salts with organic acids it is frequently most convenient to convert into carbonate of potassa by long-continued gentle ignition in covered crucibles. If they are heated to fusion, the separated carbon acts on the carbonate of potassa; carbonic oxide escapes, and a portion of caustic potassa is produced. A slight loss of potassa is occasioned by simple carbonization; a further loss takes place on fusion, which is consequently to be avoided.

b. Estimation.

Potassa is weighed either as *sulphate* or *nitrate of potassa*, or as *chloride of potassium* or *bichloride of platinum and chloride of potassium*, or precipitated and estimated volumetrically as *silicofluoride of potassium.* For the alkalimetric estimation of caustic or carbonated potassa, see §§ 219 and 220. The estimation of potash as the bitartrate, which gives approximate results only, will be found in the Special Part.

We may convert into

1. SULPHATE OF POTASSA: Salts of potassa with strong volatile acids; *e.g.*, chloride of potassium, bromide of potassium, nitrate of potassa, &c.; also salts of organic acids.

2. NITRATE OF POTASSA: Caustic potassa, and compounds of potassa with weak volatile acids that are not decomposed by nitric acid; *e.g.*, carbonate of potassa (salts of potassa with organic acids).

3. CHLORIDE OF POTASSIUM: In general, caustic potassa and salts of potassa with weak volatile acids, especially also with such as are decomposed by nitric acid; *e.g.*, sulphide of potassium. Also, and more particularly, sulphate, chromate, chlorate, and silicate of potassa.

4. BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM: Salts of potassa with acids soluble in alcohol, especially with non-

volatile acids; *e.g.*, phosphate of potassa, borate of potassa; also in the separation of potassa from soda.

5. SILICOFLUORIDE OF POTASSIUM: Salts of potassa with acids soluble in weak alcohol, except the borate.

1. *Determination as Sulphate of Potassa.*

Evaporate the aqueous solution of the sulphate of potassa to dryness, ignite the residue in a platinum crucible or dish, and weigh (§ 42). The residue must be thoroughly dried before you proceed to ignite it; the heat applied for the latter purpose must be moderate at first, and very gradually increased to the requisite degree; the crucible or dish must be kept well covered—neglect of these precautionary rules involves always a loss of substance from decrepitation. If free sulphuric acid is present, we obtain, upon evaporation, bisulphate of potassa; in such cases the excess of sulphuric acid is to be removed by igniting first alone (here it is best to place the lamp so that the flame may strike the cover obliquely from above), then with carbonate of ammonia. See § 68.

For properties of the residue, see § 68. Observe more particularly that the residue must dissolve to a clear fluid, and that the solution must be neutral. Should traces of platinum remain behind (the dish not having been previously weighed) these must be determined, and their weight subtracted from that of the ignited residue.

With proper care and attention, this method gives accurate results.

To convert the above-mentioned salts (chloride of potassium, &c.) into sulphate of potassa, add to their aqueous solution a quantity of pure sulphuric acid more than sufficient to saturate the whole of the potassa, evaporate the solution to dryness, ignite the residue, and convert the bisulphate of potassa into the neutral salt, by treating with carbonate of ammonia (§ 68).

As the expulsion of a large quantity of sulphuric acid is a very disagreeable process, avoid adding too great an excess. Should too little of the acid have been used, which you may infer from the non-evolution of sulphuric acid fumes on ignition, moisten the residue with dilute sulphuric acid, evaporate, and again ignite. If you have to deal with a small quantity only of chloride of potassium, &c., proceed at once to treat the dry salt, cautiously, with dilute sulphuric acid in the platinum crucible, provided the latter be capacious enough. In the case of bromide and iodide of potassium, the use of platinum vessels must be avoided.

Potassa salts of organic acids are carbonized in a platinum crucible at the lowest possible temperature; after cooling, a few crystals of pure sulphate of ammonia are added, then a little water; the water and the carbonate of ammonia formed are evaporated by heating the lid, and afterwards the excess of sulphate of ammonia is driven off by gently heating the bottom of the crucible. If the carbon is not all burnt, add small quantities of nitrate of ammonia till this result is effected. Weigh the sulphate of potassa remaining (H. KAMMERER*). It is usually advisable to ignite finally in an atmosphere of carbonate of ammonia. Results accurate.

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* Zeitschr. f. anal. Chem. 7, 221.

2. *Determination as Nitrate of Potassa.*

General method the same as in 1. Nitrate of potassa must be heated very gently to the fusing point, otherwise some loss is likely to arise from evolution of oxygen. For properties of the residue, see § 68. The method is easy, and the results accurate. In the conversion of carbonate of potassa into the nitrate, § 38 must be consulted.

3. *Determination as Chloride of Potassium.*

General method the same as in 1. The residue of chloride of potassium must, previously to ignition, be treated in the same way as sulphate of potassa, and for the same reason. The salt must be heated in a well-covered crucible or dish, and only to dull redness, as the application of a higher degree of heat is likely to cause some loss by volatilization. No particular regard need be had to the presence of free acid. For properties of the residue, see § 68. This method, if properly and carefully executed, gives very accurate results. The chloride of potassium may, instead of being weighed, be determined volumetrically by § 141, *b.* This method, however, has no advantage in the case of single estimations, but saves time when a series of estimations has to be made.

In determining potassa in the carbonate it is sometimes desirable to avoid the effervescence occasioned by treatment with hydrochloric acid, as, for instance, in the case of the ignited residue of a potassa salt with an organic acid, which is contained in the crucible. This may be effected by treating the carbonate with solution of chloride of ammonium in excess, evaporating and igniting, when carbonate of ammonia and the excess of chloride of ammonium will escape, leaving chloride of potassium behind.

The methods of converting into chloride of potassium the potassa compounds specified above, will be found in Part II. of this Section, under the heads of the acids which they contain.

4. *Determination as Bichloride of Platinum and Chloride of Potassium.*

a. Salts of potassa with volatile acids (nitric acid, acetic acid, &c.).

Mix the solution with hydrochloric acid, evaporate to dryness, dissolve the residue in a little water, and add a concentrated solution of bichloride of platinum, as neutral as possible, in excess. If the strength of the platinum solution is known, it will be easy to add about the right quantity (§ 63, 8). Evaporate in a porcelain dish, on the water-bath, nearly to dryness, taking care not to heat the water-bath quite to boiling. Pour spirit of wine of about 80 per cent. over the residue, mix with care; let it stand for some time, and then transfer the bichloride of platinum and chloride of potassium, which remains undissolved, to a weighed filter (which may be readily done by means of a washing bottle filled with spirit of wine). Wash with spirit of wine, dry at 130°, and weigh. An asbestos filtering tube (fig. 68, p. 79) is generally to be recommended. After the fluid has been removed as much as possible from the tube by suction, it is dried by being inserted in a somewhat wider tube, about 4 cm. shorter, which is fixed in the air-bath (fig. 38, p. 48). Air is then slowly drawn through the tube, while the air-bath is heated, finally at 130° for a considerable time. The current of air should be dried by concentrated sulphuric acid, and should enter the tube at the wide end. When the drying is finished, and the tube is weighed, it is easy to convert the precipitate into platinum by way of control. For this purpose hydrogen is transmitted through the tube while it is heated with the lamp. The chloride of potassium is then extracted with water, the tube is dried again, and the platinum is weighed, 1 eq. = 1 eq. potassium.

If a paper filter is used, dry it first at 100° and weigh, then determine the loss of weight at 130° by taking some of the same paper, and calculate what the filter would weigh at 130°.

β. Potassa salts with non-volatile acids (phosphoric acid, boracic acid, &c.).

Make a concentrated solution of the salt in water, add some hydrochloric acid, and bichloride of platinum in excess, mix with a tolerable quantity of the strongest alcohol, let the mixture stand 24 hours; after which filter, and proceed as directed in *α*.

Properties of the precipitate, § 68. This method, if properly executed, gives satisfactory results. Still there is generally a trifling loss of substance, bichloride of platinum and chloride of potassium not being absolutely insoluble even in strong alcohol. In accurate analyses, therefore, the alcoholic washings must be evaporated, with addition of water and a little pure chloride of sodium, at a temperature not exceeding 75°, nearly to dryness, and the residue treated once more with spirit of wine. A trifling additional amount of bichloride of platinum and chloride of potassium is thus obtained, which is either added to the principal precipitate or collected on a separate small filter, and determined as platinum, by the method given below. The object of the addition of a little chloride of sodium to the bichloride of platinum is to obviate the decomposition to which pure bichloride of platinum is more liable, upon evaporation in alcoholic solution, than the bichloride containing sodio-bichloride of platinum. The atmosphere of a laboratory often contains ammonia, which might give rise to the formation of some chloride of platinum and ammonium, and to a consequent increase of weight in the potassium salt.

As collecting a precipitate upon a weighed paper filter is a rather tedious process, and, besides, not over accurate, where we have to deal with minute quantities of substance, it is better, if we do not prefer a filtering tube, to collect small portions (up to about ·03 grm.) of bichloride of platinum and chloride of potassium upon a very small unweighed filter,—dry, and transfer the filter, with the precipitate wrapped up in it, to a small porcelain crucible. Cover the crucible, and let the filter slowly char; remove the cover, burn the carbon of the filter, and let the crucible get cold. Put now a very minute portion of pure oxalic acid into the crucible, cover, and ignite, gently at first, finally to a strong red heat. The addition of the oxalic acid greatly promotes the complete decomposition of the bichloride of platinum and chloride of potassium, which cannot well be effected by simple ignition. It need hardly be mentioned that a current of hydrogen may be substituted for the oxalic acid. Treat the contents of the crucible now with water, and wash the residuary platinum, preferably by decantation, until the last rinsings remain clear upon addition of nitrate of silver. Dry the residuary platinum, ignite, and weigh.

5. *Estimation as Silicofluoride of Potassium.*

To the moderately concentrated solution of the potash salt in a beaker add a sufficiency of hydrofluosilicic acid,* and then an equal volume of pure strong spirit. If the potash salt was difficultly soluble (such as bichloride of platinum and chloride of potassium), warm it with the hydrofluosilicic acid before adding the spirit. The silicofluoride of potassium will separate as a translucent precipitate; when it has settled, filter, wash out the beaker with a mixture of equal parts strong spirit and water, and wash the precipitate with the same mixture till the washings are no longer acid to litmus paper. Put the filter and precipitate into the beaker previously used, treat with water, add some tincture of litmus, heat to boiling, and add normal alkali solution (§ 215), or, in the case of small quantities, decinormal alkali solution, till the fluid is just blue, and remains so after continued boiling. The reaction is as follows:—$KF,SiF_2 + 2KO = 3KF + SiO_2$, consequently 2 eq. alkali in the standard solution correspond to 1 eq. potash originally present and precipitated as silicofluoride of potassium (Fr. Stolba†).

If the solution of the potash salt contains much free acid, particularly sulphuric acid, this is to be removed by heat before adding the hydrofluosilicic acid. Small quantities of ammonia salts are of no influence, large quantities should be removed. It need hardly be mentioned that other metals precipitable by hydrofluosilicic acid must be absent. The results are satisfactory. Stolba obtained 99·2 to 100 per cent. The bichloride of platinum and chloride of potassium may be easily converted into silicofluoride of potassium; hence, in technical analyses, the potash may be separated in the first form, and then titrated as the latter (Stolba, *loc. cit.*).

§ 98.

2. Soda.

a. Solution.

See § 97, *a*, all the directions given in that place applying equally to the solution of soda and its salts.

b. Determination.

Soda is determined either as *sulphate of soda* or *nitrate of soda*, or as *chloride of sodium* or as *carbonate of soda* (§ 69). For the alkalimetric estimation of caustic soda and carbonate of soda, see §§ 219 and 220.

We may convert into

1. Sulphate of soda; 2. Nitrate of soda; 3. Chloride of sodium: in general the salts of soda corresponding to the salts of potassa specified under the analogous potash compounds, § 97.

4. Carbonate of soda: caustic soda, bicarbonate of soda, and salts of soda with organic acids, also nitrate of soda and chloride of sodium.

5. Silicofluoride of sodium: salts of soda with acids soluble in weak spirit, except the borate.

In the borate of soda the alkali is estimated best as sulphate (§ 136); in the phosphate, as chloride, nitrate, or carbonate (§ 135).

Salts of soda with organic acids are determined either, like the corresponding potassa compounds, as sulphate, chloride, or nitrate; or—by preference—as carbonate. (This latter method is not so well adapted for salts of potassa.) The analyst must here bear in mind, that when carbon acts on fusing carbonate of soda, carbonic oxide escapes, and caustic soda in not inconsiderable quantity is formed.

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* W. Knop and W. Wolf use hydrofluosilicate of aniline instead.—Zeitschr. f. anal. Chem. 1, 471.

† Zeitschr. f. anal. Chem. 3, 298.

1. *Determination as Sulphate of Soda.*

If alone and in aqueous solution, evaporate to dryness, ignite and weigh the residue in a covered platinum crucible (§ 42). The process does not involve any risk of loss by decrepitation, as in the case of sulphate of potassa. If free sulphuric acid happens to be present, this is removed in the same way as in the case of sulphate of potassa.

With regard to the conversion of chloride of sodium, &c., into sulphate of soda, see under *Potassa.* For properties of the residue, see § 69. The method is easy, and gives accurate results.

2. *Determination as Nitrate of Soda.*

Same method as in 1. The rules given and the observations made under *Potassa,* apply equally here. For properties of the residue, see § 69.

3. *Determination as Chloride of Sodium.*

Same method as in 1. The rules given and the observations made under *Potassa,* apply equally here. Chloride of sodium is more difficultly volatilized than chloride of potassium. For properties of the residue see § 69.

The methods of converting the sulphate, chromate, chlorate, and silicate of soda into chloride of sodium, will be found in Part II. of this Section, under the heads of the acids which these salts contain.

4. *Determination as Carbonate of Soda.*

Evaporate the aqueous solution, ignite moderately, and weigh. The results are perfectly accurate. For properties of the residue, see § 69.

Caustic soda is converted into the carbonate by adding to its aqueous solution carbonate of ammonia in excess, evaporating at a gentle heat, and igniting the residue.

Bicarbonate of soda, if in the dry state, is converted into the carbonate by ignition. The heat must be very gradually increased, and the crucible kept well covered. If in aqueous solution, it is evaporated to dryness in a capacious silver or platinum dish, and the residue ignited

Salts of soda with organic acids are converted into the carbonate by ignition in a covered platinum crucible. The heat must be increased very gradually. When the mass has ceased to swell, and the carbonization is ended, add water, warm, filter off the carbon, wash it, evaporate the filtrate and washings to dryness with addition of carbonate of ammonia, and ignite the residue. The carbonate of ammonia is to reconvert any soda that may have formed into carbonate. The method, if carefully conducted, gives accurate results; however, a small loss of soda on carbonization is not to be avoided. The carbon on the filter is to be burnt. If any residue remains soluble in water, dissolve it and add it to the principal solution.

Nitrate of soda, or chloride of sodium, may be converted into carbonate, by adding to their aqueous solution perfectly pure oxalic acid in moderate excess, and evaporating several times to dryness, with repeated renewal of the water. All the nitric acid of the nitrate of soda escapes in this process (partly decomposed, partly undecomposed); and equally so all the hydrochloric acid in the case of chloride of sodium. If the residue is now ignited until the excess of oxalic acid is removed, carbonate of soda is left.

§ 99.

3. AMMONIA.

a. Solution.

Ammonia is soluble in water, as are all its salts with those acids which claim our attention here. It is not always necessary, however, to dissolve the ammoniacal salts for the purpose of determining the amount of ammonia contained in them.

b. Determination.

Ammonia is weighed, as stated, § 70, either in the form of *chloride of ammonium*, or in that of *bichloride of platinum and chloride of ammonium*. Into these forms it may be converted either directly or indirectly (*i.e.*, after expulsion as ammonia, and re-combination with an acid). Occasionally it is determined by separation as platinum salt, and weighing the platinum. It is also frequently determined by volumetric analysis, and its quantity is sometimes inferred, from the volume of nitrogen.

We convert directly into

1. CHLORIDE OF AMMONIUM: Ammonia and its aqueous solution, and also ammoniacal salts with weak volatile acids (carbonate of ammonia, sulphide of ammonium, &c.).

2. BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM: Ammoniacal salts with acids soluble in alcohol, such as sulphate of ammonia, phosphate of ammonia, &c.

3. The methods based on the EXPULSION OF THE AMMONIA from its compounds, and also that of inferring the amount of ammonia from the volume of nitrogen are equally applicable to all ammoniacal salts.

The expulsion of ammonia in the dry way (by ignition with soda-lime), and the estimation of that alkali from the volume of nitrogen eliminated in the dry way, being effected in the same manner as the estimation of the nitrogen in organic compounds, I refer the student to the Section on organic analysis. The estimation of ammonia by decomposing its compounds with a bromized solution of hypochlorite of soda, will be given under the *Analysis of Soils* in the Special Part. For the alkalimetric estimation of free ammonia, see §§ 219 and 220. For the colorimetric method depending on the use of NESSLER's solution, see the *Analysis of Water* (§ 205).

1. *Determination as Chloride of Ammonium.*

Evaporate the aqueous solution of the chloride of ammonium on the water-bath, and dry the residue at 100° until the weight remains constant (§ 42). The results are accurate. The volatilization of the chloride is very trifling. A direct experiment gave 99·94 instead of 100. (See Expt. 15.) The presence of free hydrochloric acid makes no difference; the conversion of caustic ammonia into chloride of ammonium may accordingly be effected by supersaturating with hydrochloric acid.* The same applies to conversion of the carbonate, with this addition only, that the process of supersaturation must be conducted in an obliquely-placed flask, and the mixture heated in the same, till the carbonic acid is driven off. In the analysis of sulphide of ammonium we proceed in the same way, taking care simply, after the expulsion of the sulphuretted hydrogen, and before proceeding to evaporate, to filter off the sulphur which may have separated. Instead of weighing the chloride of ammonium, its quantity may be inferred by the determination of its chlorine according to § 141, *b*. (Comp. chloride of potassium, § 97, 3.)

2. *Determination as Bichloride of Platinum and Chloride of Ammonium.*

a. Ammoniacal salts with volatile acids.

Same method as in § 97, 4, *a*.*

β. Ammoniacal salts with non-volatile acids.

Same method as in § 97, 4, *β*. The results obtained by these methods are accurate.

If you wish to control the results, ignite the double chloride, and calculate the amount of ammonia from that of the residuary platinum. The results must agree. If the double salt is in a filtering tube, pass a slow current of air through it, and heat very cautiously with the lamp. If the double salt is in paper, it is best to wrap it in the filter, place it in a crucible, heat it with the lid on for some time moderately, and then removing the lid and supporting the crucible obliquely to raise the heat gradually and burn the charred filter (H. Rose). If the double salt is pure, which may be known from its color and general appearance, this control is unnecessary. Want of due caution in heating is apt to lead to loss, from particles of the double salt being carried away with the chloride of ammonium. Very small quantities of bichloride of platinum and chloride of ammonium are collected on an unweighed filter, dried, and at once reduced to platinum by ignition.†

3. *Estimation by Expulsion of the Ammonia in the Wet Way.*

This method, which is applicable in all cases, may be effected in three different ways.

a. EXPULSION OF THE AMMONIA BY DISTILLATION WITH POTASSA, SODA, MILK OF LIME, OR MAGNESIA.—The latter is used in the presence of nitrogenous organic matter, which might yield ammonia on boiling with alkalies or lime.

Weigh the substance in a small tube 3 cm. long and 1 cm. wide, and transfer the tube and substance to a small tubulated retort *a* (fig. 78), containing a suitable quantity of moderately strong potash, soda, milk of lime, or magnesia mixed with water, which should have been previously boiled for some time to drive out every trace of ammonia, and then allowed to cool thoroughly. The further arrangement of the apparatus will be understood from the figure. The distillate must not come in contact with any cork or india-rubber, which would be liable to retain some of it.

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* Gunning (Zeitschr. f. anal. Chem.) has pointed out that fluids may become contaminated during evaporation with ammonia from the presence of the latter in coal gas.

† In a series of experiments to get the platinum from pure and perfectly anhydrous ammonio-bichloride of platinum, by cautious ignition, Mr. Lucius, one of my pupils, obtained from 44·1 to 44·3 per cent. of the metal, instead of 44·3.

If you wish to *determine volumetrically the quantity of ammonia expelled*, introduce the principal portion of a measured quantity of standard hydrochloric, sulphuric or oxalic acid (§ 215), into the receiver, the remainder into the U-tube; add to the latter a little water, and color the liquids in the receiver and U-tube red with tincture of litmus. The cooling tube must not dip into the fluid in the receiver; the fluid in the U-tube must completely fill the lower part, but it must not rise high, as otherwise the passage of air bubbles might easily occasion loss by spirting. The quantity of acid used must of course be more than sufficient to fix the whole of the ammonia expelled.

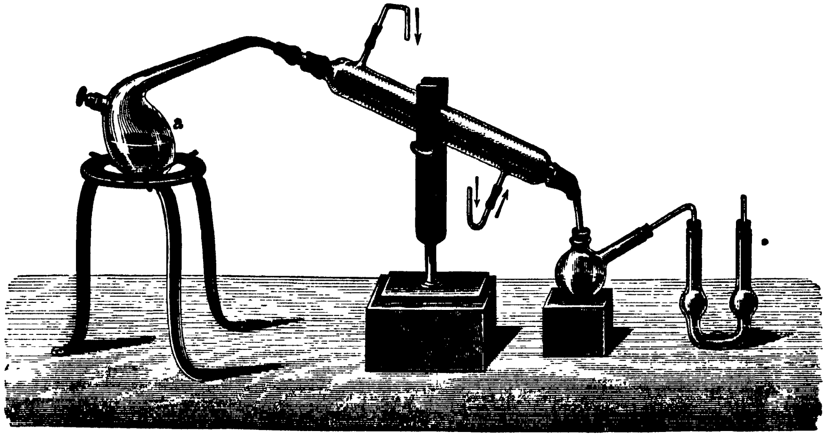

Fig. 78.

When the apparatus is fully arranged, and you have ascertained that all the joints are perfectly tight, heat the contents of the retort to gentle ebullition, and continue the application of the same degree of heat until the drops, as they fall into the receiver, have for some time altogether ceased to impart the least tint of blue to the portion of the fluid with which they first come in contact. Before ceasing to heat, fix a strip of turmeric paper in the tubulure of the retort and satisfy yourself that it is not turned brown. Loosen the stopper of the retort, allow to stand half an hour, pour the contents of the receiver and U-tube into a beaker, rinsing out with small quantities of water, determine finally with a standard solution of soda the quantity of acid still free, which, by simple subtraction, will give the amount of acid which has combined with the ammonia; and from this you may now calculate the amount of the latter (§ 220). Results accurate. (Expt. No. 55.)

If you wish to *determine by the gravimetric method the quantity of ammonia expelled*, receive the ammonia evolved in a quantity of hydrochloric acid more than sufficient to fix the whole of it, and determine the chloride of ammonium formed, either by simple evaporation after the directions of 1, or as ammonio-bichloride of platinum after the directions of 2. The latter method is much to be preferred.

b. EXPULSION OF THE AMMONIA BY MILK OF LIME, WITHOUT APPLICATION OF HEAT.—This method, recommended by SCHLÖSING, is based upon the fact that an aqueous solution containing free ammonia gives off the latter completely, and in a comparatively short time, when exposed in a shallow vessel to the air, at the common temperature. It finds application in cases where the presence of organic nitrogenous substances, decomposable by boiling alkalies or alkaline earths, forbids the use of the method described in 3, *a*; thus, for instance, in the estimation of the ammonia in urine, &c.

The fluid containing the ammonia, the volume of which must not exceed 35 c.c., is introduced into a shallow flat-bottomed vessel from 10 to 12 centimetres in diameter; this vessel is put on a plate filled with mercury. A tripod, made of a massive glass rod, is placed in the vessel which contains the solution of the ammoniacal salt, and a saucer or shallow dish with 10 c.c. of normal oxalic or sulphuric acid (§ 215) put on it. A beaker is now inverted over the whole. The beaker is lifted up on one side as far as is required, and a sufficient quantity of milk of lime added by means of a pipette (which should not be drawn out at the lower end). The beaker is then rapidly pressed down, and weighted with a stone slab. After forty-eight hours the glass is lifted up, and a slip of moist reddened litmus paper placed in it; if no change of color is observable, this is a sign that the expulsion of the ammonia is complete; in the contrary case, the glass must be replaced. Instead of the beaker and plate with mercury, a bell-jar, with a ground and greased rim, placed air-tight on a level glass plate, may be used. A bell-jar, having at the top a tubular opening, furnished with a close-fitting glass stopper, answers the purpose best, as it permits the introduction of a slip of red litmus paper suspended from a thread; thus enabling the operator to see whether the combination of the ammonia with the acid is completed, without the necessity of removing the bell-jar. According to SCHLÖSING, forty-eight hours are always sufficient to expel ·1 to 1 gramme of ammonia from 25 to 35 c.c. of solution. However, I can admit this statement only as regards quantities up to ·3 grm.; quantities above this often require a longer time. I, therefore, always prefer operating with quantities of substance containing not more than ·3 grm. ammonia.

When all the ammonia has been expelled, and has entered into combination with the acid, the quantity of acid left free is determined by means of standard solution of soda, and the amount of the ammonia calculated from the result (§ 220).

c. INDIRECT METHOD AFTER FR. MOHR.*—In this method a known quantity of alkali, in excess, is heated with water and the ammonia salt till all the ammonia has escaped, the alkali in the residue is then estimated volumetrically, and the ammonia equivalent to the alkalinity lost is calculated. The method has but limited application, since it can only be used in the analysis of neutral ammonia salts in the absence of organic matter.† It is however convenient and exact, and may be conducted in a simple flask supported obliquely. As alkali you may use either normal soda solution or normal carbonate of soda solution (53·04 grm. in 1 litre). The boiling should be stopped when the fumes escaping cease to act on litmus and turmeric paper.

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* His Lehrbuch der Titrirmethode.

† Even organic matter free from nitrogen has an injurious action, as when boiled with alkali it will yield humus-like products of decomposition with an acid nature.

§ 100.

Supplement to the First Group.

LITHIA.

In the absence of other bases, lithia may, like potassa and soda, be converted into anhydrous SULPHATE, and weighed in that form (LiO,SO_3). As lithia forms no acid sulphate, the excess of sulphuric acid may be readily removed by simple ignition. CARBONATE OF LITHIA also, which is difficultly soluble in water, and fuses at a red heat without decomposition, is well suited for weighing; whilst chloride of lithium, which deliquesces in the air, and is by ignition in moist air converted into hydrochloric acid and lithia, is unfit for the estimation of lithia.

In presence of other alkalies, lithia is best converted into BASIC PHOSPHATE OF LITHIA ($3LiO,PO_5$), and weighed in that form. This is effected by the following process: add to the solution a sufficient quantity of phosphate of soda (which must be perfectly free from phosphates of the alkaline earths), and enough soda to keep the reaction alkaline, and evaporate the mixture to dryness; pour water over the residue, in sufficient quantity to dissolve the soluble salts with the aid of a gentle heat, add an equal volume of solution of ammonia, digest at a gentle heat, filter after twelve hours, and wash the precipitate with a mixture of equal volumes of water and solution of ammonia. Evaporate the filtrate and first washings to dryness, and treat the residue in the same way as before. If some more phosphate of lithia is thereby obtained, add this to the principal quantity. The process gives, on an average, 99·61 for 100 parts of lithia (MAYER*).

If the quantity of lithia present is relatively very small, the larger portion of the potassa or soda compounds should first be removed by addition of absolute alcohol to the most highly concentrated solution of the salts (chlorides, bromides, iodides, or nitrates, but not sulphates); since this, by lessening the amount of water required to effect the separation of the phosphate of lithia from the soluble salts, will prevent loss of lithia (W. MAYER†).

The precipitated basic phosphate of lithia has the formula $3LiO, PO_5 + aq$. It dissolves in 2539 parts of pure, and 3920 parts of ammoniated water; at 100° it completely loses its water; if pure, it does not cake at a moderate red heat (MAYER).

The objections raised by RAMMELSBERG‡ to MAYER's method of estimating lithia I find to be ungrounded. According to my own experience, it appears that the filtrate and wash-water must be evaporated in a platinum dish not only once, but at least twice—in fact, till a residue is obtained which is completely soluble in dilute ammonia. Phosphate of lithia may be dried at 100°, or ignited according to § 53, before being weighed. In the latter case, care must be taken to free the filter as much as possible from the precipitate before proceeding to incinerate it. I have thus obtained,§ instead of 100 parts carbonate of lithia, by drying, 99·84, 99·89, 100·41,—by igniting, 99·66 and 100·05. The phosphate of lithia obtained was free from soda.

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* Annal. d. Chem. u. Pharm. 98, 212.

† Annal d. Chem. u. Pharm. 98, 193, where MAYER has also demonstrated the non-existence of a phosphate of soda and lithia of fixed composition (BERZELIUS), or of varying composition (RAMMELSBERG).

‡ Pogg. Annal. 102, 443.

§ Zeitschr. f. Analyt. Chem. 1, 42.

SECOND GROUP.

BARYTA—STRONTIA—LIME—MAGNESIA.

§ 101.

1. BARYTA.

a. Solution.

Caustic baryta is soluble in water, as are many of the salts of this alkaline earth. The salts of baryta which are insoluble in water are, with almost the single exception of the sulphate and silicofluoride readily dissolved by dilute hydrochloric acid. The solution of the sulphate is effected by fusion with the mixed carbonates of soda and potassa, &c. (See § 132.) Silicofluoride of barium may be readily converted into the sulphate by heating and evaporating with moderately dilute sulphuric acid in a platinum dish; it may also be conveniently decomposed by fusing with carbonate of potassa and soda.

b. Determination.

Baryta is weighed either as *sulphate*, or as *carbonate*, rarely (in the separation from strontia, &c.) as *silicofluoride of barium* or as *chromate of baryta* (§ 71). Baryta in the pure state, or in form of carbonate, may also be determined by the alkalimetric method. Comp. § 223.

We may convert into

1. SULPHATE OF BARYTA :

a. By Precipitation.—All compounds of baryta without exception.

b. By Evaporation.—All compounds of baryta with volatile acids, if no other non-volatile body is present.

2. CARBONATE OF BARYTA :

a. All salts of baryta soluble in water.

b. Salts of baryta with organic acids.

Baryta is both precipitated and weighed, by far the most frequently as sulphate, the more so as this is the form in which it is most conveniently separated from other bases. The determination by means of evaporation is, in cases where it can be applied, and where we are not obliged to evaporate large quantities of fluid, very exact and convenient. Baryta is determined as carbonate in the wet way, when from any reason it is not possible or not desirable to precipitate it as sulphate. If a fluid or dry substance contains bodies which impede the precipitation of the baryta as sulphate or carbonate (alkaline citrates, metaphosphoric acid, see § 71, *a* and *b*), such bodies must of course be got rid of, before proceeding to precipitation. The precipitation of baryta as silicofluoride and as chromate will be described under the separation from strontia, § 154.

1. *Determination as Sulphate of Baryta.*

a. By Precipitation.

Heat the moderately dilute solution of baryta, which must not contain too much free acid (and must, therefore, if necessary, first be freed therefrom by evaporation or addition of ammonia), in a platinum or porcelain dish, or in a glass vessel, to incipient ebullition, add dilute sulphuric acid, as long as a precipitate forms, keep the mixture for some time at a temperature very near the boiling point, stirring if not on a water bath, and allow the precipitate to subside; decant the almost clear supernatant fluid on a filter, boil the precipitate once with water and a little dilute sulphuric acid, then three or four times with water, transfer it to the filter, and wash with boiling water, until the filtrate is no longer rendered turbid by chloride of barium. Dry the precipitate, and treat it as directed in § 53, using only a moderate red heat. If the precipitate has been properly washed in the manner here directed, it is perfectly pure. However, in the presence of alkaline salts the precipitate will still contain small quantities of alkaline sulphate, see § 153.

b. By Evaporation.

Add to the solution, in a weighed platinum dish, pure sulphuric acid very slightly in excess, and evaporate on the water-bath; expel the excess of sulphuric acid by cautious application of heat, and ignite the residue moderately.

For the properties of sulphate of baryta, see § 71.

Both methods, if carefully executed, give almost absolutely accurate results.

2. *Determination as Carbonate of Baryta.*

a. In Solutions.

Mix the moderately dilute solution of the baryta salt, in a beaker with ammonia, add carbonate of ammonia in slight excess, and let the mixture stand several hours in a warm place. Filter, wash the precipitate with water mixed with a little ammonia, dry, and ignite moderately (§ 53).

For the properties of the precipitate, see § 71. This method involves a trifling loss of substance, as the carbonate of baryta is not absolutely insoluble in water. The direct experiment, No. 56, gave 99·79 instead of 100. If the solution contains a notable quantity of ammoniacal salts, the loss incurred is much more considerable, since the presence of such salts greatly increases the solubility of the carbonate of baryta.

b. In Salts of Baryta with Organic Acids.

Heat the salt slowly in a covered platinum crucible, until no more fumes are evolved; place the crucible obliquely, with the lid leaning against it, and ignite, until the whole of the carbon is consumed, and the residue presents a perfectly white appearance: moisten the residue with a concentrated solution of carbonate of ammonia, evaporate, ignite gently, and weigh. The results obtained by this method are quite satisfactory. A direct experiment, No. 57, gave 99·61 instead of 100. The loss of substance, which almost invariably attends this method, is owing to particles of the salt being carried away upon ignition, and is accordingly the less considerable, the more slowly and gradually the heat is increased. Omission of the moistening of the residue with carbonate of ammonia would involve a further loss of substance, as the ignition of carbonate of baryta in contact with carbon is attended with formation of some caustic baryta, carbonic oxide being evolved.

§ 102.

2. STRONTIA.

a. Solution.

See the preceding paragraph (§ 101, *a*), the directions there given applying equally here. Silicofluoride of strontium is readily and completely soluble in water acidified with hydrochloric acid.

b. Determination.

Strontia is weighed either as *sulphate* or as *carbonate of strontia* (§ 72). Strontia in the pure state, or in form of carbonate, may be determined also by the alkalimetric method. Comp. § 223.

We may convert into

1. SULPHATE OF STRONTIA:

a. By Precipitation.—All compounds of strontia without exception.

b. By Evaporation.—All salts of strontia with volatile acids, if no other non-volatile body is present.

2. CARBONATE OF STRONTIA:

a. All compounds of strontia soluble in water.

b. Salts of strontia with organic acids.

The method based on the precipitation of strontia with sulphuric acid yields accurate results only in cases where the fluid from which the strontia is to be precipitated may be mixed, without injury, with alcohol. Where this cannot be done, and where the method based on the evaporation of the solution of strontia with sulphuric acid is equally inapplicable, the conversion into the carbonate ought to be resorted to in preference, if admissible. As in the case of baryta, so here, we have to be on our guard against the presence of substances which would impede precipitation.

1. *Determination as Sulphate of Strontia.*

a. By Precipitation.

Mix the solution of the salt of strontia (which must not be too dilute, nor contain much free hydrochloric or nitric acid) with dilute sulphuric acid in excess, in a beaker, and add, at least an equal volume of alcohol; let the mixture stand twelve hours, and filter; wash the precipitate with dilute spirit of wine, dry and ignite (§ 53).

If the circumstances of the case prevent the use of alcohol, the fluid must be precipitated in a tolerably concentrated state, a good excess of sulphuric acid must be used (in the presence of chloride of potassium, sodium or magnesium this is particularly necessary), and the mixture must be allowed to stand in the cold for at least twenty-four hours, filtered, and the precipitate washed with cold water, until the last rinsings manifest no longer an acid reaction, and leave no perceptible residue upon evaporation. If traces of free sulphuric acid remain adhering to the filter, the latter turns black on drying, and crumbles to pieces; too protracted washing of the precipitate, on the other hand, tends to increase the loss of substance.

Care must be taken that the precipitate be thoroughly dry, before proceeding to ignite it; otherwise it will be apt to throw off fine particles during the latter process. The filter, which is to be burnt apart from the precipitate, must be as clean as possible, or some loss of substance will be incurred; as may be clearly seen from the depth of the carmine tint of the flame with which the filter burns if the precipitate has not been properly removed.

For the properties of the precipitate, see § 72. When alcohol is used and the directions given are properly adhered to, the results are very accurate; when the sulphate of strontia is precipitated from an aqueous solution, on the contrary, a certain amount of loss is unavoidable, as sulphate of strontia is not absolutely insoluble in water. The direct experiments, without the use of alcohol (No. 58), gave only 98·12 and 98·02 instead of 100. However, the error may be satisfactorily rectified, by calculating the amount of sulphate of strontia dissolved in the filtrate and the wash-water, basing the calculation upon the known degree of solubility of sulphate of strontia in acidified and pure water. See Expt. No. 59, which, with this correction, gave 99·77 instead of 100. The necessity for making the correction may be obviated by washing with 1 part of sulphuric acid mixed with 20 parts water till all substances precipitable by spirit are removed, then with spirit till all the sulphuric acid is removed. Sulphate of strontia also carries down, if not to the same extent as sulphate of baryta, the sulphates of other strong bases in small quantity. Compare § 153.

b. By Evaporation.

The same method as described for baryta, § 101, 1, *b.*

2. *Determination as Carbonate of Strontia.*

a. In Solutions.

The same method as described § 101, 2, *a.* For the properties of the precipitate, see § 72. The method gives very accurate results, at least far more accurate than the determination with sulphuric acid in aqueous solution when no correction is made; as carbonate of strontia is practically insoluble in water containing ammonia and carbonate of ammonia. A direct experiment, No. 60, gave 99·82 instead of 100. Presence of ammoniacal salts exercises here a less adverse influence than in the precipitation of carbonate of baryta.

b. In Salts with Organic Acids.

The same method as described § 101, 2, *b.* The remarks made there, respecting the accuracy of the results, apply equally here.

§ 103.

3. LIME.

a. Solution.

See § 101, *a.*—Fluoride of calcium is, by means of sulphuric acid, converted into sulphate of lime, and the latter again, if necessary, decomposed by boiling or fusing with an alkaline carbonate (§ 132).

b. Determination.

Lime is weighed either as *sulphate*, as *carbonate of lime*, or as *caustic lime* (§ 73). It may be brought into the first form by evaporation, or by precipitation; into the two latter, by precipitation as oxalate, or as carbonate, or by ignition. Lime in the pure state, or in form of carbonate, may be determined also by the alkalimetric method. Comp.

§ 223. The volumetric estimation may also be easily made if the lime is precipitated as oxalate, either by a direct or an indirect method.

We may convert into

1. SULPHATE OF LIME.

a. By Precipitation: All salts of lime with acids soluble in alcohol, provided no other substance insoluble in alcohol be present.

b. By Evaporation: All salts of lime with volatile acids, provided no non-volatile body be present.

2. CARBONATE OF LIME, OR LIME.

a. By Precipitation with carbonate of ammonia: All salts of lime soluble in water.

b. By Precipitation with oxalate of ammonia: All salts of lime soluble in water or in hydrochloric acid without exception.

c. By Ignition: Salts of lime with organic acids.

Of these several methods, 2, *b*, is the one most frequently resorted to. This, and the method 1, *b*, give the most accurate results. The method, 1, *a*, is usually resorted to only to effect the separation of lime from other bases; 2, *a*, generally only to effect the separation of lime together with other alkaline earths from the alkalies. As many bodies (alkaline citrates, and metaphosphates) interfere with the precipitation of lime by the precipitants given, these, if present, must be first removed.

3. The VOLUMETRIC modes of estimation, which are particularly to be recommended when a considerable number of determinations are required, will be described after the gravimetric modes.

1. *Determination as Sulphate of Lime.*

a. By Precipitation.

Mix the solution of lime, which may contain a little free hydrochloric acid, in a beaker, with dilute sulphuric acid in excess, and add three or four volumes of alcohol; let the mixture stand twelve hours, filter, and *thoroughly* wash the precipitate with spirit of wine, dry, and ignite moderately (§ 53). For the properties of the precipitate, see § 73. The results are only slightly too low. A direct experiment, No. 61, gave 99·64 instead of 100.

b. By Evaporation.

The same method as described § 101, 1, *b*.

2. *Determination as Carbonate of Lime, or Lime.*

a. By Precipitation with Carbonate of Ammonia.

The same method as described § 101, 2, *a*. The precipitate must be exposed only to a very gentle red heat, but this must be continued for some time. For the properties of the precipitate, see § 73. This method gives very accurate results, the loss of substance incurred being hardly worth mentioning. If the solution contains chloride of ammonium or similar ammoniacal salts in considerable proportion, the loss of substance incurred is far greater. The same is the case if the precipitate is washed with pure instead of ammoniacal water. A direct experiment, No. 62, in which pure water was used, gave 99·17 instead of 100 parts of lime. If it is feared that any caustic lime has formed through the heat being too high, moisten the residue with water, add a lump of carbonate of ammonia, allow to evaporate slowly, and heat again to gentle redness, that is, till the bottom of the crucible is just dull red. If a gas blowpipe can be used, the carbonate of lime may be converted into lime by prolonged strong ignition, and weighed as such; compare *b.*[*]

b. By Precipitation with Oxalate of Ammonia.

a. The Lime Salt is soluble in Water.

To the hot solution in a beaker, add oxalate of ammonia in moderate excess, and then ammonia sufficient to impart an ammoniacal smell to the fluid; cover the glass, and let it stand in a warm place until the precipitate has completely subsided, which will require twelve hours, at least. Pour the clear fluid cautiously, so as to leave the precipitate undisturbed, on a filter; wash the precipitate two or three times by decantation with hot water; lastly, transfer the precipitate also to the filter, by rinsing with hot water, taking care, before the addition of a fresh portion, to wait until the fluid has completely passed through the filter.[†] Small particles of the precipitate, adhering firmly to the glass, are removed with a feather, or a glass rod covered at the end with a piece of flexible tube. If this fails to effect their complete removal, they should be dissolved in a few drops of highly dilute hydrochloric acid, ammonia added to the solution, and the oxalate obtained, after it has settled, added to the first precipitate. Deviations from the rules laid down here will generally give rise to the passing of a turbid fluid through the filter. After having washed the precipitate, dry it on the filter in the funnel, and transfer the dry precipitate to a platinum crucible, taking care to remove it as completely as possible from the filter; burn the filter on the lid or on a piece of platinum wire, letting the ash drop into the lid; now put the latter, inverted, on the crucible, so that the filter ash may not mix with the precipitate; heat at first very gently, then more strongly, until the bottom of the crucible is heated to very faint redness. Keep it at that temperature from ten to fifteen minutes, removing the lid from time to time. I am accustomed during this operation to move the lamp backwards and forwards under the crucible with the hand, since, if you allow it to stand, the heat may very easily get too high. Finally allow to cool in the desiccator and weigh. After weighing, moisten the contents of the crucible, which must be perfectly white, or barely show the least tinge of gray, with a little water, and test this after a time with a minute slip of turmeric paper. Should the paper turn brown—a sign that the heat applied was too strong—rinse off the fluid adhering to the paper with a little water, into the crucible, throw in a small lump of pure carbonate of ammonia, evaporate to dryness (best on the water-bath), heat to very faint redness, and weigh the residue. If the weight has increased, repeat the same operation until the weight remains constant. This method gives nearly absolutely accurate results; and if the application of heat is properly managed, there is no need of the tedious evaporation with carbonate of ammonia. For the properties of the precipitate and residue, see § 73. A direct experiment, No. 63, gave 99·99 instead of 100. Equally accurate results have been obtained by A. **Souchay** in my laboratory.*

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[*] FRITZSCHE (Zeitschr. f. anal. Chem. 3, 179) and A. COSSA (*Ib.* 8, 141) in converting precipitated carbonate of lime into lime obtained somewhat too little (about 99·7 instead of 100). But I think this may be explained by supposing that the carbonate of lime employed (FRITZSCHE dried his at 160°) was not anhydrous, which FRITZSCHE himself hints.

[†] In order to make the oxalate of lime settle more rapidly and to filter it off clear more readily, MUCK recommends the addition of 1 c.c. of ammonia alum solution, containing ·001 grm. alumina. An excess of ammonia must be avoided, and ·001 must be deducted from the weight of lime obtained (Zeitschr. f. anal. Chem. 9, 451).

If a gas blowpipe is at hand, or any other arrangement by means of which a platinum crucible may be raised to a white heat, the oxalate of lime may be converted into CAUSTIC LIME with results almost equally accurate; and I believe that this method, which requires less patience than the other, is more certain to yield good results in the hands of many persons. The oxalate of lime and the filter ash are transferred to a moderate-sized platinum crucible, which is ignited first over the **Bunsen**, and then for fifteen minutes over the blowpipe. The crucible is then weighed, and ignited again for ten minutes more over the blowpipe. *The second ignition over the blowpipe should not reduce the weight. It is well to weigh the empty crucible again at the end of the operation*, as platinum sometimes loses weight after violent and prolonged ignition. The results obtained by **Fritzsche**, **Cossa**, and **Souchay** (*loc. cit.*) scarcely differ from the calculated numbers. For properties of lime, see § 73.

The oxalate of lime may also be converted into SULPHATE. **Schrötter** ignites in a covered platinum crucible with pure sulphate of ammonia. Or you may ignite in a covered platinum dish till the precipitate is for the most part converted into lime, add a little water, then hydrochloric acid to effect solution, then pure sulphuric acid in excess, evaporate and ignite moderately. This process is also quite accurate.

Many chemists collect the oxalate on a weighed filter, dry at 100°, and weigh. The precipitate consists of $2CaO,C_4O_6+2aq$. This is, however, more troublesome, and less accurate than the first method.

β. The Salt is insoluble in Water.

Dissolve the salt in dilute hydrochloric acid. If the acid combined with the lime is of a nature to escape in this operation (*e.g.*, carbonic acid), or to admit of its separation by evaporation (*e.g.*, silicic acid), proceed, after the removal of the acid, as directed in *a*. But if the acid cannot thus be readily got rid of (*e.g.*, phosphoric acid), proceed as follows: add ammonia until a precipitate begins to form, redissolve this with a drop of hydrochloric acid, add oxalate of ammonia in excess, and finally acetate of soda; allow the precipitate to subside, and proceed for the remainder of the operation as directed in *a*. In this process the free hydrochloric acid present combines with the ammonia and soda of the oxalate and acetate, liberating a corresponding quantity of oxalic acid and acetic acid, in which acids oxalate of lime is nearly insoluble. The loss by this method is very slight. A direct experiment, No. 64, gave 99·78 instead of 100.

c. By Ignition.

The same method as described § 101, 2, *b*. The residue remaining upon evaporation with carbonate of ammonia (which operation it is advisable to perform twice) must be ignited very gently. The remarks made in reference to the accuracy of the results, apply equally here. By way of control, the carbonate of lime may be converted into the caustic state or into sulphate of lime (see *b*, *a*), or it may be determined alkalimetrically (§ 223).

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* Zeitschr. f. anal. Chem. 10, 323.

3. *Volumetric Methods.*

a. For the *alkalimetric estimation* of caustic lime and carbonate of lime, see § 223. Very good results may be obtained from the mixture of lime and carbonate of lime, produced by igniting the oxalate moderately in the air (Expt. No. 65).

b. Precipitation as oxalate and direct estimation of the oxalic acid. The precipitate is well washed, but not dried, and the oxalic acid is estimated by permanganate of potassa (§ 137); 9 parts of anhydrous oxalic acid represent 7 parts of lime (HEMPEL). Results very good (Expt. No. 65).

c. Precipitation as oxalate and indirect estimation of the oxalic acid (KRAUT*). The lime salt must be soluble in water. Place the solution in a measuring flask, add an exactly measured quantity of decinormal oxalic acid (§ 215), more than sufficient to precipitate the lime, add ammonia till alkaline, boil, allow to cool, fill the flask up to the mark, shake, filter through a dry filter, measure out an aliquot part of the filtrate (not less than one-half), and determine the oxalic acid in it by permanganate of potash, according to § 137; calculate the quantity for the whole filtrate, deduct this from the quantity added, and the remainder will be the oxalic acid equivalent to the lime present. 1 c.c. decinormal oxalic acid = ·0028 grm. lime. This process is rapid, and gives good results. If the amount of lime is small in comparison with the volume of the fluid no correction will be necessary on account of the space occupied by the oxalate of lime in the measuring flask.

§ 104.

4. MAGNESIA.

a. Solution.

Many of the compounds of magnesia are soluble in water; those which are insoluble in that menstruum dissolve in hydrochloric acid, with the exception of some silicates and aluminates (see §§ 105 and 140).

b. Determination.

Magnesia is weighed (§ 74) as *sulphate*, as *pyrophosphate*, or as *pure magnesia*. In the pure state, or in form of carbonate, it may be determined also by the alkalimetric method described in § 223.

We may convert into

1. SULPHATE OF MAGNESIA: All compounds of magnesia with volatile acids, provided no other non-volatile substance be present.

2. PYROPHOSPHATE OF MAGNESIA: All compounds of magnesia without exception.

3. PURE MAGNESIA:

a. Salts of magnesia with organic acids, or with readily volatile inorganic oxygen acids.

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* Chem. Centralbl. 1856, 316.

b. Chloride of magnesium, and the compounds of magnesia convertible into that salt.

The direct determination as sulphate of magnesia is highly recommended in all cases where it is applicable. The determination as pyrophosphate is most generally resorted to; especially also in the separation of magnesia from other bases. The method based on the conversion of chloride of magnesium into pure magnesia is usually resorted to only to effect the separation of magnesia from the fixed alkalies. Compounds of magnesia with phosphoric acid are analysed as § 135 directs.

1. *Determination as Sulphate of Magnesia.*

Add to the solution pure dilute sulphuric acid in quantity more than sufficient to combine with the magnesia present, evaporate to dryness, in a weighed platinum dish on the water bath; then heat at first cautiously, afterwards, with the cover on more strongly—here it is advisable to place the lamp so that the flame may play obliquely on the cover from above—until the excess of sulphuric acid is completely expelled; lastly, ignite gently over the lamp for some time; allow to cool, and weigh. Should no fumes of sulphuric acid escape upon the application of a strongish heat, this may be looked upon as a sure sign that the sulphuric acid has not been added in sufficient quantity, in which case, after allowing to cool, a fresh portion of sulphuric acid is added. The method yields very accurate results. Care must be taken not to use a very large excess of sulphuric acid. The residue must be exposed to a moderate red heat only, and weighed rapidly. For the properties of the residue, see § 74.

2. *Determination as Pyrophosphate of Magnesia.*

The solution of the salt of magnesia is mixed, in a beaker, with chloride of ammonium, and ammonia added in slight excess. Should a precipitate form upon the addition of ammonia, sufficient chloride of ammonium must be added to effect its re-solution. The clear fluid is then mixed with a solution of phosphate of soda in excess, and the mixture stirred, taking care to avoid touching the sides of the beaker with the stirring-rod; otherwise particles of the precipitate are apt to adhere so firmly to the rubbed parts of the beaker, that it will be found difficult to remove them; the beaker is then covered, and allowed to stand at rest for twelve hours, without warming; after that time the fluid is filtered, and the precipitate collected on the filter, the last particles of it being rinsed out of the glass with a portion of the filtrate, with the aid of a feather; when the fluid has completely passed through, the precipitate is washed with a mixture of 3 parts of water, and 1 part of solution of ammonia of ·96 sp. gr., the operation being continued until a few drops of the fluid passing through the filter mixed with nitric acid and a drop of nitrate of silver show no opalescence. The precipitate is now thoroughly dried, and then transferred to a platinum crucible (§ 53); the latter, with the lid on, is exposed for some time to a very gentle heat, which is finally increased to intense redness. The filter, as clean as practicable, is incinerated on the lid, and the ash transferred to the crucible, which is then once more exposed to a red heat, allowed to cool, and weighed. If the pyrophosphate of magnesia is not quite white, moisten it with a few drops of nitric acid, evaporate them off, and heat the residue again, using great caution at first.

For the properties of the precipitate and residue, see § 74. This method, if properly executed, yields most accurate results. The precipitate must be washed completely, but not over-washed, and the washing water must always contain the requisite quantity of ammonia.

3. *Determination as pure Magnesia.*

a. In Salts of Magnesia with Organic or Volatile Inorganic Acids.

The salt of magnesia is gently heated in a covered platinum crucible, increasing the temperature gradually, until no more fumes escape; the lid is then removed, and the crucible placed in an oblique position, with the lid leaning against it. A red heat is now applied, until the residue is perfectly white. For the properties of the residue, see § 74. The method gives the more accurate results the more slowly the salt is heated from the beginning. Some loss of substance is usually sustained, owing to traces of the salt being carried off with the empyreumatic products. Salts of magnesia with readily volatile oxygen acids (carbonic acid, nitric acid), may be transformed into magnesia in a similar way, by simple ignition. Even sulphate of magnesia loses the whole of its sulphuric acid when exposed, in a platinum crucible, to the heat of the gas blowpipe-flame (SONNENSCHEIN). As regards small quantities of sulphate of magnesia, I can fully confirm this statement.

b. Conversion of Chloride of Magnesium into pure Magnesia.

The concentrated solution of chloride of magnesium is mixed in a porcelain crucible, with pure oxide of mercury shaken up with water, in proportion more than sufficient to convert by its oxygen the whole of the magnesium present into magnesia. The mixture is evaporated on the water-bath, and the residue thoroughly dried; the crucible is now covered, and exposed to a red heat, until the chloride of mercury formed is expelled, together with the excess of oxide of mercury. The operator should carefully guard against inhaling the fumes evolved. The residue of magnesia is either weighed at once in the crucible, or if the operation had for its object the separation of the earth from the alkalies, it is collected upon a filter, washed with hot water, dried, and ignited (§ 53). Compare also § 153, B, 4 (**17**–**21**), where some other methods are given to effect the same purpose, which are often more convenient for separation.

THIRD GROUP OF THE BASES.

ALUMINA—SESQUIOXIDE OF CHROMIUM—(TITANIC ACID).

§ 105.

1. ALUMINA.

a. Solution.

Those of the compounds of alumina which are insoluble in water, dissolve, for the most part, in hydrochloric acid. Native crystallized alumina (sapphire, ruby, corundum), and many native alumina compounds, and also artificially produced alumina after intense ignition, require fusing with carbonate of soda, caustic potassa, or hydrate of baryta, as a preliminary step to their solution in hydrochloric acid. Many alumina compounds (*e.g.*, clay) which resist the action of concentrated hydrochloric acid, may be decomposed by protracted heating with moderately concentrated sulphuric acid, or by fusion with bisulphate of soda. Bisulphate of potassa used to be employed, but it gives rise to the formation of a troublesome double salt of alumina and potassa difficultly soluble in water and acids (L. SMITH*).

b. Determination.

Alumina is almost invariably weighed in the *pure state*, occasionally as *phosphate* (compare for instance § 209, 7, II.). The several compounds of alumina are converted into pure alumina, either by precipitation as hydrate of alumina, and subsequently ignition, or by simple ignition. Precipitation as basic acetate or basic formiate is resorted to only in cases of separation. For an indirect (acidimetric) estimation of alumina in alum, &c., see § 215.

We may convert into

ALUMINA:

a. By Precipitation. All compounds of alumina soluble in water, and those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid.

b. By Heating or Ignition. *α.* All salts of alumina with readily volatile oxygen acids (*e.g.*, nitrate of alumina). *β.* All salts of alumina with organic acids.

With regard to the method *a*, it must be remembered that the solution must contain no organic substances, which would interfere with the precipitation—*e.g.*, tartaric acid, sugar, &c. Should such be present, the solution must be mixed with carbonate of soda and nitrate of potassa, evaporated to dryness in a platinum dish, the residue fused, then macerated in water, transferred to a beaker, digested with hydrochloric acid, and the solution filtered, and then precipitated.

The methods *b*, *α* and *β*, are applicable only in cases where no other fixed substances or chloride of ammonium are present. (The latter when ignited with alumina would occasion a loss of chloride of aluminium.) The methods of estimating alumina in its combinations with phosphoric, boracic, silicic, and chromic acids, will be found in Part II. of this Section, under the heads of these several acids.

Determination as Alumina.

a. By Precipitation.

Mix the moderately dilute hot solution of alumina with a tolerable quantity of chloride of ammonium, if that salt is not already present, add ammonia in *slight* excess, heat to boiling and maintain at that temperature till the free ammonia is completely or very nearly expelled—*i.e.*, till the fluid gives a neutral or barely alkaline reaction (the fluid adhering to the test paper must be washed back again). The fluid should not be heated too long, or it will become acid through decomposition of the chloride of ammonium, and some of the alumina will redissolve. The most appropriate vessel for the precipitation is a large platinum dish, in default of which a porcelain dish may be used; glass should not be employed, as it is attacked by hot ammoniacal fluids

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* Am. Journ. of Science and Arts, 40, 248.

(p. 65). Allow to settle, decant the clear supernatant fluid through a filter, without disturbing the precipitate, pour boiling water on the latter, stir it up, allow to settle again, pour off the clear fluid through the filter, and repeat this washing a second and a third time, finally transfer the precipitate to the filter and wash it thoroughly with boiling water. Suction is particularly useful in this case (§ 47); if it is employed, the precipitate may be ignited by the method given p. 85, immediately after washing. If suction is not employed, the ignition of the moist precipitate is rather a critical operation. If you wish to dry the precipitate before you ignite it, let it be as dry as possible, and then ignited according to § 52. Apply a very gentle heat at first, and keep the crucible well covered, or you may easily lose small quantities by the violent escape of the last portions of water retained by the alumina.

In whichever way the precipitate is ignited it is always best to expose it to an incipient white heat over the gas blowpipe for some time, in order to be sure that the last trace of water is expelled (A. MITSCHERLICH*). This is the more necessary, and the heat must be continued five or ten minutes when the solution contained *sulphuric acid*, as the precipitate then contains basic sulphate of alumina, which requires very strong and prolonged ignition for its decomposition. In default of a gas blowpipe, the precipitate, either simply washed or moderately ignited, must be redissolved in hydrochloric acid (which requires protracted warming with strong acid), and then precipitated again with ammonia; or the sulphate must first be converted into nitrate by decomposing it with nitrate of lead, added in very slight excess, the excess of lead removed by means of hydrosulphuric acid, and the further process conducted according to the directions of *a* or *b*. Carbonate of ammonia or sulphide of ammonium may be used instead of ammonia for precipitating, but without increasing the accuracy of the results. For the properties of hydrate of alumina and ignited alumina, see § 75. Never neglect to test the alumina for silicic acid, which it frequently contains. This is done readily by heating with dilute sulphuric acid or fusing with bisulphate of potassa or soda (§ 75). The method, if properly executed, gives very accurate results. But if a considerable excess of ammonia is used, more particularly in the absence of ammoniacal salts, and the liquid is filtered without boiling or long standing in a warm place to remove the ammonia, no trifling loss may be incurred. This loss is the greater, the more dilute the solution, and the larger the excess of ammonia. The precipitate cannot be well sufficiently washed on the filter on account of its gelatinous nature; on the other hand, if it be entirely washed by decantation, a very large quantity of wash-water must be used, hence it is advisable to combine the two methods, as directed.

b. By Ignition.

α. Compounds of alumina with volatile acids.—Ignite the salt (or the residue of the evaporated solution) in a platinum crucible, gently at first, then gradually to the very highest degree of intensity, until the weight remains constant. For the properties of the residue, see § 75. Its purity must be carefully tested. There are no sources of error.

β. Compounds of alumina with organic acids.—The same method as described § 104, 3, *a* (MAGNESIA).

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* Zeitschr. f. anal. Chem. 1, 67.

§ 106.

2. SESQUIOXIDE OF CHROMIUM.

a. Solution.

Many of the compounds of sesquioxide of chromium are soluble in water. The hydrated sesquioxide, and most of the salts insoluble in water, dissolve in hydrochloric acid. Ignition renders sesquioxide of chromium and many of its salts insoluble in acids; this insoluble modification must be prepared for solution in hydrochloric acid, by fusing with three or four parts of potassa in a silver crucible. A small quantity is converted, in the process of fusing, into chromic acid, by the action of the air; this is, however, reduced again to sesquioxide upon heating with hydrochloric acid. Addition of alcohol greatly promotes the reduction. Instead of this fusing with potassa, we frequently prefer to adopt a treatment, whereby the sesquioxide is at once oxidized and converted into an alkaline chromate (see 2). For the solution of chromic iron, see § 160.

b. Determination.

Sesquioxide of chromium is always, when directly determined, weighed in the *pure state*. It is brought into this form either by precipitation as hydrate and ignition, or by simple ignition. It may, however, also be estimated, by conversion into chromic acid, and determination as such.

We may convert into

1. SESQUIOXIDE OF CHROMIUM:

a. By Precipitation. All compounds of sesquioxide of chromium soluble in water, and also those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid. Provided always that no organic substances (such as citric acid, tartaric acid, oxalic acid, &c.) which interfere with the precipitation be present.

b. By Ignition. α. All salts of sesquioxide of chromium with volatile oxygen acids, provided no non-volatile substances be present. β. Salts of sesquioxide of chromium with organic acids.

2. CHROMIC ACID, or, more correctly speaking, ALKALINE CHROMATE: Sesquioxide of chromium and all its salts.

The methods of analysing the combinations of the sesquioxide of chromium with chromic acid, phosphoric acid, boracic acid, and silicic acid, will be found in Part II. of this Section, under the heads of these several acids.

1. *Determination as Sesquioxide of Chromium.*

a. By Precipitation.

A platinum dish should be used by preference; porcelain may also be used, but not glass. The solution, which must not be too highly concentrated, is heated to 100°. Ammonia is then added slightly in excess, and the mixture exposed to a temperature approaching boiling, until the fluid over the precipitate is perfectly colorless, presenting no longer the least shade of red; let the solid particles subside, wash three times by decantation, and lastly on the filter, with hot water, dry thoroughly, and ignite (§ 52). The heat in the latter process must be increased gradually, and the crucible kept covered, otherwise some loss of substance is likely to arise from spirting upon the incandescence of the sesquioxide of chromium which marks the passing of the soluble into the insoluble modification. The precipitate may also be very conveniently washed by suction (§ 47), and may then be transferred, still moist, to the crucible in which it is to be ignited and weighed. For the properties of the precipitate and residue, see § 76. This method, if properly executed, gives accurate results. When a porcelain dish is used, the results are only very slightly too high, in consequence of the contamination of the precipitate with silicic acid; when a glass vessel is used, the contamination of the precipitate is very decided (A. SOUCHAY*). Sulphide of ammonium may be used instead of ammonia for precipitating. In this case no heat is required, and glass vessels may be used.

b. By Ignition.

α. Salts of sesquioxide of chromium with volatile acids. The same method as described, § 105 (*Alumina*).

β. Salts of sesquioxide of chromium with organic acids. The same method as described § 104 (*Magnesia*).

2. CONVERSION OF SESQUIOXIDE OF CHROMIUM INTO CHROMIC ACID.

(For the estimation of chromic acid, see § 130.)

The following methods have been proposed with this view :—

a. The solution of the salt of sesquioxide of chromium is mixed with solution of potassa or soda in excess, until the hydrated sesquioxide, which forms at first, is redissolved. Chlorine gas is then conducted into the cold fluid until it acquires a yellowish-red tint; it is then mixed with potassa or soda in excess, and the mixture evaporated to dryness; the residue is ignited in a platinum crucible. The whole of the chlorate of potassa (or soda) formed is decomposed by this process, and the residue consists, therefore, of alkaline chromate and chloride (VOHL).

b. Hydrate of potassa is heated in a silver crucible to calm fusion; the heat is then somewhat moderated, and the perfectly dry compound of sesquioxide of chromium projected into the crucible. When the sesquioxide of chromium is thoroughly moistened with the potassa, small lumps of fused chlorate of potassa are added. A lively effervescence ensues, from the escape of oxygen; at the same time the mass acquires a more and more yellow color, and finally becomes clear and transparent. Loss of substance must be carefully guarded against (H. SCHWARZ).

c. Dissolve the sesquioxide of chromium in solution of potassa or soda, add binoxide of lead in sufficient excess, and warm. The yellow fluid produced contains all the chromium as chromate of lead in alkaline solution. Filter from the excess of binoxide of lead, add to the filtrate acetic acid to acid reaction, and determine the weight of the precipitated chromate of lead (G. CHANCEL†).

d. Mix the sesquioxide of chromium in a fine state of division with chlorate of potassa in a porcelain dish, add nitric acid of 1·367 sp. gr., cover the dish with a funnel of somewhat smaller diameter, heat on a water bath, and from time to time add crystals of chlorate of potassa till all the sesquioxide is dissolved and converted into chromic acid.

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* Zeitschr. f. anal. Chem. 4, 66.

† Comp. rend. 43, 927.

Even with sesquioxide, which has been very strongly ignited, the operation does not last more than 30 or 60 minutes. The chromic acid in the solution thus obtained may be conveniently determined as chromate of baryta (STORER,* PEARSON†).

§ 107.

Supplement to the Third Group.

TITANIC ACID.

Titanic acid is always weighed in the pure state; its separation is effected either by precipitation with an alkali, by heating with alkaline acetate, or by boiling the dilute acid solution. Titanic acid may also be estimated volumetrically. In *precipitating* acid solutions of titanic acid ammonia is employed; take care to add the precipitating agent only in slight excess, let the precipitate formed, which resembles hydrate of alumina, deposit, wash, first by decantation, then completely on the filter, dry, and ignite (§ 52). If the solution contained sulphuric acid, put some carbonate of ammonia into the crucible, after the first ignition, to secure the removal of every remaining trace of that acid. Lose no time in weighing the ignited titanic acid, as it is slightly hygroscopic. Occasionally it is more convenient to precipitate the titanic acid from its acid solution by nearly neutralizing with ammonia, adding acetate of soda or ammonia and boiling. The precipitate thus obtained is easily filtered off and washed. If we have titanic acid dissolved in sulphuric acid, or if it is dissolved by fusing with bisulphate of potassa, and treating the mass with cold water, the titanic acid may be precipitated by largely diluting and boiling for a long time with renewal of the evaporating water; and the precipitate thus obtained may be easily washed with water. If much free acid is present, the greater part of it should be neutralized with ammonia before commencing to boil. The operation is best conducted in a platinum dish. After filtering, add more ammonia to the filtrate to neutralize the acid still further, and boil again for some time to see whether any more titanic acid will be precipitated. By testing the last filtrate with ammonia, you may make quite sure that the precipitation is complete. When igniting the dried precipitate, add a little carbonate of ammonia. If you attempt to precipitate the titanic acid in a similar way from dilute hydrochloric solutions, it does not separate entirely until the fluid is evaporated to dryness, and it must be washed with water containing a little acid, or the washings will pass turbid through the filter.

Hydrate of titanic acid precipitated in the cold, washed with cold water and dried without heat, is completely soluble in hydrochloric acid; under other conditions it is not completely soluble. The hydrate of metatitanic acid, precipitated by boiling dilute acid solutions, is insoluble in dilute acids. Ignited titanic acid is insoluble even in concentrated hydrochloric acid, but it does dissolve on prolonged heating with moderately strong sulphuric acid. It is easily dissolved by fusing for a long time with bisulphate of potassa, and treating the mass with much cold water. Upon fusing with carbonate of soda, titanate of soda is formed, which, when treated with water, leaves acid titanate of soda, a salt soluble in hydrochloric acid. By fusing titanic acid with three times its quantity of fluoride of potassium and hydrogen, fluoride of titanium and potassium is formed, which readily dissolves in very dilute hydrochloric acid (of sp. gr. 1·015) in the heat. On fusing a very low heat must be applied at first, till the excess of hydrofluoric acid has escaped, then the heat is quickly raised till the mass melts and the titanic acid is just dissolved (MARIGNAC*). Titanic acid contains 60·98 per cent. of titanium and 39·02 of oxygen. On heating with hydrofluoric and sulphuric acids practically no fluoride of titanium escapes, but by heating with hydrofluoric acid some loss does occur (RILEY†).

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* Zeitschr. f. anal. Chem. 9, 71.

† *Ib.* 9, 108.

Titanic acid may be estimated *volumetrically* by being first reduced to sesquioxide, and then oxidized to titanic acid by standard solution of permanganate of potash (comp. § 112, 2; PISANI‡). Sulphuric acid solutions are to be avoided, either the ordinary hydrochloric solution is taken, or the solution of the fluoride of titanium and potassium in dilute hydrochloric acid. The reduction is effected by zinc with exclusion of air, with or without the application of a gentle heat. In the case of hydrochloric solutions it is accompanied with violet coloration, in the case of fluoride of titanium and potassium with greenish coloration. The reduction being complete the zinc is removed, and the permanganate is added to incipient reddening of the fluid. The weak point of the method lies in the difficulty of knowing exactly when the reduction is finished. MARIGNAC§ has described the conditions under which he almost invariably obtained good results.

FOURTH GROUP OF THE BASES.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—SESQUIOXIDE OF IRON—(SESQUIOXIDE OF URANIUM).

§ 108.

1. OXIDE OF ZINC.

a. Solution.

Many of the salts of zinc are soluble in water. Metallic zinc, oxide of zinc, and the salts, which are insoluble in water, dissolve in hydrochloric acid. Hydrochloric acid is also the best solvent for precipitated sulphide of zinc. For blende the best method is first to digest in a finely-divided state with concentrated hydrochloric acid in the heat, and then to add a little nitric acid, chlorate of potassa, or solution of bromine in hydrochloric acid.

b. Determination.

Zinc is weighed either as *oxide* or *sulphide* (§ 77). The conversion of the salts of zinc into the oxide is effected either by precipitation as basic carbonate or sulphide of zinc, or by direct ignition. Beside these gravimetric methods, several volumetric methods are in use.

We may convert into

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* Zeitschr. f. anal. Chem. 7, 112.

† *Ib.* 2, 71.

‡ *Ib.* 4, 419.

§ *Ib.* 7, 113.

1. OXIDE OF ZINC:

a. By Precipitation as carbonate of zinc. All the salts of zinc which are soluble in water, and all those with organic volatile acids; also those salts of zinc which, insoluble in water, dissolve in hydrochloric acid, with separation of their acid.

b. By Precipitation as sulphide of zinc. All compounds of zinc without exception.

c. By direct Ignition. Salts of zinc with volatile inorganic oxygen acids.

2. SULPHIDE OF ZINC: All compounds of zinc without exception.

The method 1, *c*, is to be recommended only, as regards the more frequently occurring compounds of zinc, for the carbonate and the nitrate. The methods 1, *b*, or 2, are usually only resorted to in cases where 1, *a*, is inadmissible. They serve more especially to separate oxide of zinc from other bases. Salts of zinc with organic acids cannot be converted into the oxide by ignition, since this process would cause the reduction and volatilization of a small portion of the metal. If the acids are volatile, the zinc may be determined at once, according to method 1, *a*; if, on the contrary, the acids are non-volatile, the zinc is best precipitated as sulphide. For the analysis of chromate, phosphate, borate, and silicate of zinc, look to the several acids. The volumetric methods are chiefly employed for technical purposes; see Special Part.

1. *Determination as Oxide of Zinc.*

a. By Precipitation as Carbonate of Zinc.

The best material to use for precipitating in is platinum, porcelain may also be employed, but not glass. Heat the moderately dilute solution nearly to boiling in a *capacious* vessel; add drop by drop carbonate of soda till the fluid shows a strong alkaline reaction; boil a few minutes; allow to subside, decant through a filter, and boil the precipitate three times with water, decanting each time; then transfer the precipitate to the filter, wash completely with hot water, dry, and ignite as directed § 53, taking care to have the filter as clean as practicable, before proceeding to incinerate it. To prevent reduction of the oxide and volatilization of the metal you may, after removing the precipitate as much as possible from the filter, saturate the latter carefully with solution of nitrate of ammonia, dry it, and then incinerate it. Should the solution contain ammoniacal salts, the ebullition must be continued until, upon a fresh addition of the carbonate of soda, the escaping vapor no longer imparts a brown tint to turmeric paper. If the quantity of ammoniacal salts present is considerable, the fluid must be evaporated by *boiling* to dryness. It is, therefore, in such cases more convenient to precipitate the zinc as sulphide (see *b*).

The presence of a great excess of acid in the solution of zinc must be as much as possible guarded against, that the effervescence from the escaping carbonic acid gas may not be too impetuous. The filtrate must always be tested with sulphide (with addition of chloride) of ammonium to ascertain whether the whole of the zinc has been precipitated; the experiment should be done in a flask filled up to the neck, and closed. If the process has been properly conducted, no precipitate will be obtained here, or the precipitate will be so insignificant that it may be altogether disregarded, being limited to some exceedingly slight and imponderable flakes, which moreover make their appearance only after many hours' standing. If the precipitate is more considerable, however, it must be treated as directed in *b*, and the weight of the oxide of zinc obtained added to that resulting from the first process. For the properties of the precipitate and residue, see § 77. The results are in most cases a little too low, as the precipitation is never absolutely complete, and as particles of the precipitate will always and unavoidably adhere to the filter, which exposes them to the chance of reduction and volatilization during the process of ignition. On the other hand, the results are sometimes too high; this is owing to defective washing, as may be seen from the alkaline reaction which the residue manifests in such cases. It is advisable also to ascertain whether the residue will dissolve in hydrochloric acid without leaving silicic acid; this latter precaution is indispensable in cases where the precipitation has been effected in a glass vessel.

b. By Precipitation as Sulphide of Zinc.

Mix the solution, contained in a not too large flask and sufficiently diluted, with chloride of ammonium, then add ammonia, till the reaction is just alkaline, and then colorless or slightly yellow sulphide of ammonium in moderate excess. If the flask is not now quite full up to the neck, make it so with water, cork, allow to stand 12 to 24 hours in a warm place, wash the precipitate, if considerable, first by decantation, then on the filter with water containing sulphide of ammonium and also less and less chloride of ammonium (finally none). If the sulphide of zinc is to be weighed as such, substitute nitrate of ammonia for the chloride. In decanting do not pour the fluid through the filter, but into a flask. After thrice decanting, filter the fluid that was poured off, and then transfer the precipitate to the filter, finishing the washing as directed. The funnel is kept covered with a glass plate. If the zinc is not to be determined according to 2, then put the moist filter with the precipitate in a beaker, and pour over it moderately dilute hydrochloric acid slightly in excess. Put the glass now in a warm place, until the solution smells no longer of sulphuretted hydrogen; dilute the fluid with a little water, filter, wash the original filter with hot water, and proceed with the solution of chloride of zinc obtained as directed in *a*.

From a solution of acetate of zinc the metal may be precipitated completely, or nearly so, with sulphuretted hydrogen gas, even in presence of an excess of acetic acid, provided no other acid be present. (Expt. No. 66). The following method also effects a practically complete precipitation of zinc from acid solution. Add carbonate of soda, at last drop by drop till a lasting precipitate forms, dissolve the latter by a drop of hydrochloric acid, pass sulphuretted hydrogen till the precipitate ceases to increase perceptibly, add acetate of soda, and again pass the gas. After washing with water containing sulphuretted hydrogen (which when the sulphide of zinc had been thrown down by sulphuretted hydrogen from acetic acid solution, is easily done), treat as above directed. Small quantities of sulphide of zinc may also be converted directly into the oxide, by heating in an open platinum crucible to gentle redness at first, then, after some time, to most intense redness.

c. By direct Ignition.

The salt is exposed, in a covered platinum crucible, first to a gentle heat, finally to a most intense heat, until the weight of the residue remains constant. The action of reducing gases is to be avoided.

2. *Determination as Sulphide of Zinc.*

The precipitated sulphide of zinc, obtained as in 1, *b*, may be ignited in hydrogen and weighed. H. ROSE,* who has recommended the process, employs the following apparatus.

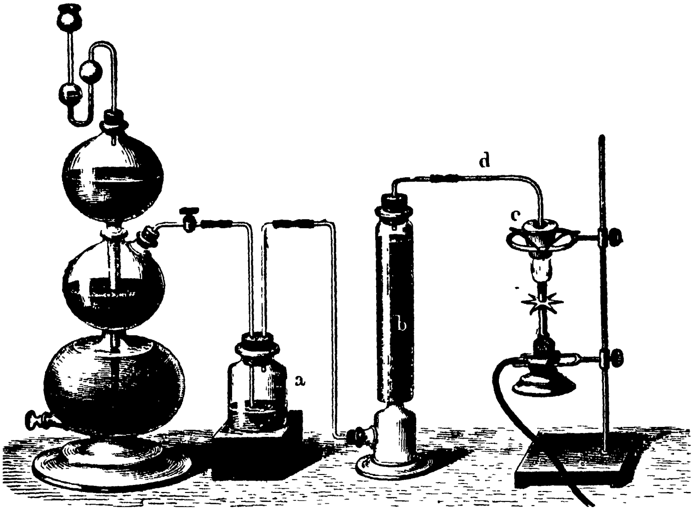

Fig. 79.

a contains concentrated sulphuric acid, *b*, chloride of calcium. The porcelain crucible has a perforated porcelain or platinum cover, into the opening of which fits the porcelain or platinum tube, *d*. The latter is provided with an annular projection which rests on the cover, the tube itself extends some distance into the crucible. When the sulphide of zinc has dried in the filter, it is transferred to the weighed porcelain crucible, the filter ash is added, powdered sulphur is sprinkled over the contents of the crucible, the cover is placed on, and hydrogen is passed in a moderate stream, a gentle heat is applied at first, which is afterwards raised to intense redness; finally, the crucible is allowed to cool with continued transmission of the gas, and the sulphide of zinc is weighed.

Instead of the above apparatus, which is not at every analyst's disposal, any apparatus may of course be used which allows the current of gas to be regulated, such as that figured p. 159 of the "Qualitative Analysis" (9th edition). An evolution apparatus, in which the current is not under control, is not so suitable. In default of a perforated crucible lid and porcelain tube you may use a short tobacco-pipe, the bowl of which fits exactly in a small porcelain crucible.

Sulphate, carbonate, and oxide of zinc, may also be converted into sulphide, as above. They must be mixed with excess of sulphur, or loss will be sustained, owing to the reducing action of the hydrogen upon oxide of zinc. Sulphate of zinc is best ignited with access of air, before being mixed with sulphur and ignited in hydrogen (H. ROSE).

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* Pogg. Annal. 110, 128.

The properties of the hydrated and anhydrous sulphide of zinc are given § 77; the results are accurate. Loss occurs only when the ignition is performed over the gas blowpipe (which is quite unnecessary), and continued longer than five minutes. Compare p. 129.

§ 109.

2. PROTOXIDE OF MANGANESE.

a. Solution.

Many of the salts of protoxide of manganese are soluble in water. The pure protoxide, and those of its salts which are insoluble in that menstruum, dissolve in hydrochloric acid, which dissolves also the higher oxides of manganese. The solution of the higher oxides is attended with evolution of chlorine—equivalent in quantity to the amount of oxygen which the oxide under examination contains, more than the protoxide of manganese—and the fluid, after application of heat, is found to contain protochloride of manganese.

b. Determination.

Manganese is weighed either as *protosesquioxide,* as *sulphide,* as *protosulphate,* or as *pyrophosphate* (§ 78). Into the form of protosesquioxide it is converted either by precipitation as carbonate, or as hydrated protoxide, sometimes preceded by precipitation as sulphide of manganese, or as binoxide of manganese; or, finally, by direct ignition. Manganese may be determined volumetrically in three different ways. The first is applicable to any solution of protoxide of manganese, provided it be free from any other substance which exerts a reducing action on alkaline solution of ferricyanide of potassium. The second requires the absence of sesquioxide of iron. The third is only admissible when we have manganese in the condition of a perfectly definite higher oxide, and free from other bodies, which evolve chlorine on boiling with hydrochloric acid.

We may convert into

1. PROTOSESQUIOXIDE OF MANGANESE:

a. By Precipitation as carbonate of manganese. All the soluble salts of manganese with inorganic acids, and all its salts with volatile organic acids; also those of its salts which, insoluble in water, dissolve in hydrochloric acid with separation of their acid.

b. By Precipitation as hydrated protoxide of manganese. All the compounds of manganese named under *a.*

c. By Precipitation as sulphide of manganese. All compounds of manganese without exception.

d. By Separation as binoxide of manganese. All compounds of manganese in a slightly acid solution, especially acetate and nitrate of protoxide of manganese.

e. By direct Ignition. All oxygen compounds of manganese; salts of manganese with readily volatile oxygen acids, and with organic acids.

2. SULPHIDE OF MANGANESE: All compounds of manganese without exception.

3. SULPHATE OF MANGANESE: All the oxides of manganese, and

likewise all its salts with volatile acids, provided no non-volatile substance be present.

4. Pyrophosphate of manganese: All salts of manganese soluble in water, and other salts whose acid may be removed by solution in acid.

The method 1, *e*, is simple and accurate, but seldom admissible. The method 1, *a*, is the most usually employed; if one's choice is free, it is to be preferred to 1, *b*. The methods 1, *c*, and 2, are generally used when the methods 1, *a*, or *b*, cannot be adopted—say on account of the presence of a non-volatile organic substance, and also when we have to separate manganese from other metals. The latter object may be attained also by the method 1, *d*. The process 3, is sometimes convenient, but it yields only approximate results. The method 4, has been much recommended recently; it is quickly executed, but only yields satisfactory results when the solubility of the phosphate of ammonia and manganese is taken into account. The phosphate and borate of manganese are treated according to the method 2, or in the first case, the method 4. In silicates the manganese is determined after the separation of the silicic acid (§ 140), according to 1, *a*; for the analysis of chromate of manganese, see § 130. The two first volumetric methods are especially suited for technical work, in which the highest degree of accuracy is not required. The estimation of manganese from the quantity of chlorine disengaged upon boiling the oxides with hydrochloric acid, is resorted to, more particularly, to determine the oxides of manganese, and permits also the estimation of manganese in presence of other metals (see Section V.).

1. *Determination as Protosesquioxide of Manganese.*

a. By Precipitation as Carbonate of Protoxide of Manganese.

The precipitation and washing are effected in exactly the same way as directed § 108, 1, *a*; a platinum or porcelain dish being used for the former. As the filtrate and washings (which sometimes show a slight turbidity) are never quite free from manganese, evaporate both in platinum or porcelain to dryness, treat the residue with boiling water, collect the undissolved flocks of hydrated protosesquioxide of manganese upon a separate small filter and wash with hot water. Now dry the two filters and ignite according to § 53, exhaust the resulting protosesquioxide of manganese repeatedly with boiling water, pouring off the water onto a small filter, incinerate this filter on a platinum wire or a crucible lid, put the ash in the crucible, and ignite strongly with the lid off in a good oxidizing flame, keeping reducing gases out of the crucible, till the weight is constant. For properties of the precipitate and residue, see § 78. When executed as directed, the method gives good results. If you neglect the small quantity of manganese in the filtrate, or if you weigh the residue without exhausting with water, although the two errors tend to neutralize each other, still you cannot expect other than approximate results. After weighing take the residue out of the platinum crucible, and see if it will dissolve in hydrochloric acid without leaving silica.

b. By Precipitation as Hydrated Protoxide of Manganese.

The solution should not be too concentrated, and it is best to have it in a platinum dish; porcelain may be used, but not glass. Precipitate with pure soda or potassa, and proceed in all other respects as in *a*. For the properties of the precipitate, see § 78. For the accuracy of the method and the testing of the residue, see *a*.

c. By Precipitation as Sulphide of Manganese.

See 2

d. By Separation as Binoxide of Manganese.

Heat the solution of the acetate of manganese or some other compound of the protoxide containing but little free acid, after addition of a sufficient quantity of acetate of soda, to from 50° to 60°, and transmit chlorine gas through the fluid, or add bromine (KÄMMERER,* WAAGE†). The manganese falls down as binoxide (SCHIEL,—RIVOT, BEUDANT, and DAGUIN). Presence of ammonia salts may render the precipitation incomplete. Wash, first by decantation, then upon the filter, dry, transfer the precipitate to a flask, add the filter ash, heat with hydrochloric acid, filter, and precipitate as directed in *a*. If the proportion between the acetate of soda and the free acid (especially if it be hydrochloric acid) is incorrect, it may happen that the precipitation of the manganese by chlorine is not quite complete, it is therefore well, after filtering off the peroxide, to add more acetate of soda to the filtrate, and again treat with chlorine or bromine. If the filtrate is pink from permanganic acid, add alcohol and heat to throw down the small remainder of the manganese. It is impossible to convert the precipitated peroxide into protosesquioxide directly by ignition, as the residue so obtained is full of alkali, and cannot be purified by washing. The separation of manganese as binoxide, by evaporating its solution in nitric acid to dryness, and heating the residue, finally to 155°, is given in Section V.

e. By direct Ignition.

The manganese compound under examination is introduced into a platinum crucible, which is kept closely covered at first, and exposed to a gentle heat; after a time the lid is taken off, and replaced loosely on the crucible, and the heat is increased to the highest degree of intensity, with careful exclusion of reducing gases; the process is continued until the weight of the residue remains constant. The conversion of the higher oxides of manganese into protosesquioxide requires more protracted and intense heating than the conversion of the protoxide. In fact, it can hardly be effected without the use of a gas blowpipe. (Hence in such cases it is best to convert into sulphide by adding sulphur, and igniting in hydrogen, see 2.) In the case of salts of manganese with organic acids, care must always be taken to ascertain whether the whole of the carbon has been consumed; and should the contrary turn out to be the case, the residue must either be dissolved in hydrochloric acid, and the solution precipitated, &c., as directed in *a*, or it must be repeatedly evaporated with nitric acid, until the whole of the carbon is oxidized. The method, if properly executed, gives accurate results. On the other hand, if the directions are not carefully attended to, one must not be surprised at considerable differences. In the ignition of salts of manganese with organic acids, there is a trifling loss generally, from the reasons stated, § 104, 3.

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* Ber. der deutsch. Chem. Gesellsch. 4, 218.

† Zeitschr. f. anal. Chem. 10, 206.

2. *Determination as Sulphide of Manganese.*

The precipitation of manganese as sulphide may be effected in two different ways; the second is to be preferred when it is desired to complete the operation with comparative rapidity.

a. The solution contained in a comparatively small flask and not too dilute is first mixed with chloride of ammonium (if an ammonia salt is not already present in sufficient quantity), then—if the fluid is acid—with ammonia, till it reacts neutral or very slightly alkaline: now add yellowish sulphide of ammonium in moderate excess, if the flask is not already quite full up to the neck, add water till it is, cork, stand it in a warm place (for at least twenty-four hours) till the supernatant fluid is perfectly clear, wash the precipitate if at all considerable, first by decantation, then on the filter, using water containing sulphide of ammonium, and also gradually diminished quantities of chloride of ammonium (finally none). In decanting, pour the fluid in a flask, not on the filter. After decanting three times, filter the fluids that have been poured off, transfer the precipitate to the filter, and finish the washing as above directed, without interruption. Keep the funnel covered with a glass plate.

b. Neutralize the fluid with ammonia, boil, add sulphide of ammonium, boil for ten minutes, allow to cool a few degrees, add more sulphide of ammonium (the fluid should now smell of the latter), and filter through a double filter. If the filtrate is turbid, pour it back till it runs through clear (R. FINKENER*). The sulphide of manganese often separates from the boiling fluid in the anhydrous state, and with a green color, especially in the absence of much ammonia salt, and the presence of much free ammonia; wash with water containing a little sulphide of ammonium.

The washed sulphide of manganese was formerly dissolved in hydrochloric acid, and reprecipitated according to 1, *a*; but it is much quicker to dry it, and ignite it strongly with the filter ash and some sulphur in a current of hydrogen till it becomes black, weighing as anhydrous sulphide (H. ROSE†), see the corresponding process for zinc, § 108, 2. For the properties of the precipitate and residue, and the circumstances which promote or hinder the precipitation, see § 78, *e.* The results obtained by OESTEN, and adduced by ROSE, are entirely satisfactory. Equally good results have been obtained by myself. When the process has been properly conducted none but the most insignificant traces of manganese will be found in the filtrate from the sulphide. Tartaric acid retards the precipitation, but does not render it less complete; citric acid prevents the precipitation, or at least makes it quite imperfect.

The sulphate and all the oxides of manganese may also be converted into the sulphide by ignition with sulphur in a current of hydrogen.

3. *Determination as Sulphate of Manganese.*

The same method as in the case of magnesia under the same circumstances; see § 104, 1. Care must be taken to avoid too great an excess of sulphuric acid, and to expose the residue to a faint red heat only. For the properties of the residue, see § 78. If accurate results are obtained, it is only by chance; as, if we heat gently, the weight is generally too high; if we heat more strongly, it is generally too low from the volatilization of sulphuric acid (H. ROSE*). To obtain satisfactory results, convert the sulphate into sulphide, as in 2.

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* Handb. d. anal. Chem. von H. ROSE, 6. Aufl. von R. FINKENER, page 925.

† Pogg. Annal. 110, 122.

4. *Estimation as Pyrophosphate of Manganese* (W. GIBBS†).

It is best to use a platinum dish for the precipitation; porcelain may be used, but not glass. To the solution add phosphate of soda in large excess, then hydrochloric acid to redissolve the precipitate, heat to incipient ebullition, add ammonia in excess, and boil ten or fifteen minutes; the precipitate is phosphate of manganese and ammonia, and it is crystalline; keep it in contact with the fluid for an hour, maintaining the latter nearly at the boiling temperature, filter, wash (according to GIBBS) with boiling water, ignite and weigh the pyrophosphate of manganese.

According to my experience it is better to filter with suction, so as to use as little water as possible, and to wash with cold instead of boiling water (§ 78). Accurate results cannot be got unless you evaporate the filtrate and washings to dryness, dissolve the residue in hydrochloric acid and water, boil, and add ammonia, &c.; *i.e.*, unless you repeat the above process to precipitate and determine the small remainder of manganese, which generally amounts to between two and four milligrammes.

If the precipitate turns dark red on the filter, it was not completely converted into the ammonia salt, and it must then be dissolved in hydrochloric acid, and subjected again to the process of precipitation with addition of more phosphate of soda.

5. *Volumetric Methods of estimating Manganese.*

a. Determination by the Reduction of Ferricyanide of Potassium (E. LENSSEN‡).

The method is grounded on the fact that if a solution of protoxide of manganese which contains 1 eq. Fe_2O_3 to 1 eq. MnO, is acted on by excess of alkaline solution of ferricyanide of potassium at a boiling temperature, all the manganese is precipitated as binoxide, while a corresponding quantity of ferrocyanide of potassium is formed. By determining the latter, the amount of manganese present is obtained.

$$K_3Cy_6Fe_2 + 2KO + MnO,SO_3 = 2K_2Cy_3Fe + KO,SO_3 + MnO_2.$$

Accordingly 1 eq. manganese gives rise to 2 eq. ferrocyanide of potassium. Of course all other reducing substances must be absent, and the manganese must be present entirely in the form of proto-salt. If the solution contains no sesquioxide of iron, the precipitate is a combination of much binoxide, with little protoxide, not always in the same proportions. In performing the process, mix first with the acid solution of protoxide of manganese so much sesquichloride of iron that you may be sure of having at least 1 eq. Fe_2O_3 to 1 eq. MnO, and add the mixture gradually to a boiling solution of ferricyanide of potassium, previously rendered strongly alkaline with potassa or soda. After boiling together a short time the brownish-black precipitate becomes granular and less bulky. Allow to cool *completely*, filter off and wash the precipitate, acidify the filtrate with hydrochloric acid, and estimate the ferrocyanide of potassium with permanganate, according to § 147 II., *g*. If the liquid is filtered hot, the results are too high, as the filter in this case has a reducing action. The method may be shortened, as follows: After boiling, transfer the solution, together with the precipitate, to a measuring flask, allow to cool, fill up to the mark with water, shake, and allow to settle. Filter through a dry filter, take out a certain quantity with a pipette, and determine the ferrocyanide in this. A slight source of error is here introduced by disregarding the volume of the precipitate. The results adduced by **Lenssen** are very satisfactory. I have myself repeatedly tested this method, and I have to remark as follows:—*a*. If ferricyanide of potassium is long boiled with pure potassa, a small quantity of ferrocyanide is invariably produced. *b*. The potassa must be quite free from organic substances, and should therefore, if there is any doubt on this point, be fused in a silver dish before use, otherwise the error alluded to in *a* may be considerably increased. *c*. The complete washing of the voluminous precipitate is attended with so much difficulty and loss of time as to render the method more troublesome than a gravimetric analysis. *d*. The abridged method, on the other hand, may be of great service in certain cases, especially when a series of manganese determinations have to be made, the manganese not being in too minute quantities, and the highest degree of accuracy not being required. In my laboratory, by employing a slight excess of sesquioxide of iron, 97·9—100·12—98·21—98·99, and 100·4 were obtained instead of 100. The inaccuracy increases on using a large excess of the iron.*

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* Pogg. Annal. 110, 125.

† Sillim. Amer. Journ. (ii.), 44, 216.

‡ Journ. f. prakt. Chem. 80, 408.

b. Estimation by precipitating the Manganese with permanganate of Potassa (A. **Guyard**†).

If a solution of permanganate of potassa acts on a dilute neutral or barely acid solution of manganese at 80°, the whole of the manganese both in the original solution and in the precipitant is thrown down as $3MnO,Mn_2O_7 + 5HO$ or (divided by 5) MnO_2HO. The end of the reaction is evidenced by the pink coloration of the fluid. The permanganate solution is standardized by iron or by manganese.

Dissolve from 1 to 2 grm. of the substance in aqua regia, boil for a short time to convert all the manganese into protochloride, nearly neutralize with an alkali, dilute largely with boiling water (1 or 2 litres), raise to a temperature of 80° and maintain at this point while you are adding the standard solution of permanganate of potassa. A brown flocculent precipitate forms immediately. Allow it to settle from time to time and conclude the operation as soon as the fluid shows a distinct red color.

The critical examination of the method undertaken in my laboratory by R. **Habich**,‡ led to the following conclusions: *a*. The results are accurate in neutral solutions. *b*. A very small quantity of free sulphuric acid distinctly increases the amount of permanganate required, but the results are still good enough for technical purposes. *c*. A larger quantity of free sulphuric acid prevents the reaction altogether. *d*. Free hydrochloric acid acts like sulphuric acid, but with greater power (its influence may be destroyed by the addition of finely divided oxide of mercury, **Winkler**§). *e*. The method is useless in the presence of sesquioxide of iron or sesquioxide of chromium. *f.* The other conditions being satisfied, the presence of nickel, cobalt, zinc, alumina, or lime does not interfere with the results.

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* Zeitschr. f. anal. Chem. 3, 209.

† Chem. News, 1863, 292.

‡ Zeitschr. f. anal. Chem. 3, 474.

§ *Ib.* 3, 423.

c. Determination by boiling the higher oxides with hydrochloric acid, and estimating the chlorine evolved.

The methods here employed will be found all together in the Special Part under "Valuation of Manganese Ores."

§ 110.

3. PROTOXIDE OF NICKEL.

a. Solution.

Many of the salts of protoxide of nickel are soluble in water. Those which are insoluble, as also the pure protoxide, in its common modification, dissolve, without exception, in hydrochloric acid. The peculiar modification of protoxide of nickel, discovered by GENTH, which crystallizes in octahedra, does not dissolve in acids, but is rendered soluble by fusion with bisulphate of potassa. Metallic nickel dissolves slowly, with evolution of hydrogen, when warmed with dilute hydrochloric or sulphuric acid; in nitric acid, it dissolves with great readiness. Sulphide of nickel is but sparingly soluble in hydrochloric acid, but it dissolves readily in nitrohydrochloric acid. Peroxide of nickel dissolves in hydrochloric acid, upon the application of heat, to protochloride, with evolution of chlorine.

b. Determination.

Nickel is weighed as protoxide, or as metal; occasionally as the anhydrous sulphate (§ 79). The compounds of nickel are converted into the protoxide, usually by precipitation as hydrated protoxide, preceded, in some instances, by precipitation as sulphide of nickel, or by ignition. Nickel may also be estimated volumetrically.

We may convert into

1. PROTOXIDE OF NICKEL.

a. By Precipitation as hydrated protoxide of nickel. All the salts of nickel with inorganic acids which are soluble in water, and all its salts with volatile organic acids; likewise all salts of nickel which, insoluble in water, dissolve in the stronger acids, with separation of their acid.

b. By Precipitation as sulphide of nickel. All compounds of nickel without exception.

c. By Ignition. The salts of nickel with readily volatile oxygen acids, or with such oxygen acids as are decomposed at a high temperature (carbonic acid, nitric acid).

2. METALLIC NICKEL: Protoxide of nickel (and all the compounds mentioned under 1, *a*, *b*, and *c*), also the compounds with chlorine, bromine, and iodine.

3. SULPHATE OF NICKEL: Salts of nickel, whose acids are entirely expelled by heating and evaporating with sulphuric acid.

The methods of preparing metallic nickel, by simply igniting the protoxide, and by igniting pure nickel compounds in a current of hydrogen, are extremely accurate, but not always applicable. The method 1, *a*, is most commonly employed, sometimes in combination with 2. In the presence of sugar, or other non-volatile organic substance, it cannot be used. In this case we must either ignite and thereby destroy the organic matter before precipitating, or we must resort to the method 1, *b*, which otherwise is hardly used except in separations. The conversion into sulphate of nickel is quickly executed, but the results are entirely trustworthy only where the greatest care is taken. The combinations of the protoxide of nickel with chromic, phosphoric, boracic, and silicic acids are analysed according to the methods given under the several acids. The volumetric methods are rarely worth using, and in point both of simplicity and exactness leave much to be desired.

1. *Determination as Protoxide of Nickel.*

a. By Precipitation as Hydrated Protoxide of Nickel.

Mix the solution with pure solution of potassa or soda in excess, heat for some time nearly to ebullition, decant four times, boiling up each time, filter, wash with hot water, dry and ignite strongly, avoiding the action of reducing gases (§ 53). The precipitation is best effected in a platinum dish; in presence of nitrohydrochloric acid, or, if the operator does not possess a sufficiently capacious dish of the metal, in a porcelain dish; glass vessels do not answer the purpose so well. Presence of ammoniacal salts, or of free ammonia, does not interfere with the precipitation. For the properties of the precipitate and residue, see § 79. This method, if properly executed, gives very accurate results. The thorough washing of the precipitate is a most essential point. It is necessary also to ascertain whether the residue has not an alkaline reaction, and whether it dissolves completely in hydrochloric acid.

b. By Precipitation as Sulphide of Nickel.

This requires the greatest care and attention. The best way is to proceed according to one of the three subjoined methods.*

α. The moderately dilute cold solution of nickel contained in a proper-sized flask is, if necessary, neutralized with ammonia (the reaction should be rather slightly acid than alkaline): chloride of ammonium is added, if it, or some other ammonia salt of similar action, such as the acetate, is not already present in sufficient quantity, and then hydrosulphate of sulphide of ammonium, as long as a precipitate is produced. The NH_4S,HS should be perfectly saturated with HS, it may be colorless or light-yellow. A large excess of the reagent must be avoided. After mixing, fill the flask with water up to the neck, cork, and allow to stand about twenty-four hours without warming, but in a moderately warm place. The precipitate has now settled, and the clear supernatant fluid is colorless or slightly yellow. Decant, filter, and wash as described in the case of sulphide of manganese (§ 109, 1, *c*). Filtrate and wash-water must be colorless or slightly yellow. Dry the precipitate in the funnel, and transfer as completely as possible from the filter, to a beaker; the filter is incinerated in a coil of platinum wire, or upon the lid of a crucible, and the ash added to the dry precipitate. The precipitate is now treated with concentrated nitrohydrochloric acid, and the mixture digested at a gentle heat, until the whole of the sulphide of nickel is dissolved, and the undissolved sulphur appears of a pure yellow, hydrochloric acid is added and the fluid is evaporated to drive off the nitric acid, it is then diluted, filtered, and the filtrate precipitated, as directed in *a*. For the properties of the precipitate, see § 79. The method, if properly executed, gives accurate results. If the solution contains free ammonia, or no salt of ammonia, the fluid filtered off from the sulphide of nickel possesses always a more or less brownish tint, and contains sulphide of nickel (§ 79, *e*), which must be regained by acidifying with acetic acid and boiling. If the precipitate is not washed as directed, some nickel is very likely to pass through with the wash-water. If the filter were not incinerated, but treated at once, together with the precipitate, with nitrohydrochloric acid, the solution of the sulphide of nickel would contain organic substances, and soda or potassa would accordingly afterwards fail to effect the complete precipitation of the nickel.

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* Another method—with hyposulphite of soda—is given, p. 134.

β. Mix the slightly acidified solution of nickel with bicarbonate of ammonia, so that the free acid may be neutralized, and the solution may contain a small excess of the bicarbonate of ammonia, together with free carbonic acid, and then pass hydrosulphuric acid gas. Precipitation will promptly ensue. Filter, and treat the precipitate as in *a*.

γ. To the solution of nickel add ammonia to alkaline reaction, then a tolerably large quantity of acetate of soda or ammonia, and sulphide of ammonium in good excess, then acetic acid to strong acid reaction, and boil. The precipitate settles well and is treated as in *a*. Test the filtrate by neutralizing with ammonia and adding sulphide of ammonium. If it turns black, acidify with acetic acid and warm to throw down the remainder of the nickel. It is not advisable to attempt to weigh the sulphide of nickel as such by ignition in hydrogen.

c. By Ignition.

Proceed as for manganese, § 109, 1, *e*.

2. *Estimation as metallic Nickel.*

Ignite the oxide or chloride to be reduced in a tall and narrow porcelain crucible in a slow stream of hydrogen (§ 108, 2), at first gently, then more strongly till the weight is constant. For properties of the residue see, § 79, *c*. If on dissolving the metal in nitric acid any silica remains, this must be weighed and deducted.

3. *Estimation as sulphate of Nickel.*

The nickel solution should be free from other non-volatile salts. Evaporate with a slight excess of pure sulphuric acid in a platinum dish to dryness and heat for 15 or 20 minutes moderately, so as just to drive off the excess of sulphuric acid without blackening the yellow sulphate at the edges. It is difficult to be sure of hitting the exact point, hence we cannot place dependence on this method nor on that of GIBBS, which consists in dissolving the sulphide in nitric acid and evaporating the solution with sulphuric acid. For the properties of the residue, see § 79, *d*.

4. *Estimation of Nickel volumetrically.*

KÜNZEL* precipitates with sulphide of sodium, using nitroprusside of sodium or ammoniacal solution of silver as indicator of the excess of the reagent. WICKE† and FLEISCHER‡ precipitate as sesquioxide by boiling with hypochlorite of soda and caustic soda and determine the precipitate by its oxidizing action on arsenious acid or protoxide of iron. **Fr. Mohr*** determines the sesquioxide by its action on iodide of potassium. **Gibbs**† precipitates with oxalic acid and alcohol and determines the oxalic acid in the precipitate with permanganate of potash.

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* Zeitschr. f. anal. Chem. 2, 373.

† *Ib.* 4, 424.

‡ *Ib.* 10, 219.

§ 111.

4. Protoxide of Cobalt.

a. Solution.

Protoxide of cobalt and its compounds behave with solvents like the corresponding compounds of nickel; metallic cobalt like metallic nickel. The protosesquioxide of cobalt obtained by **Schwarzenberg** in microscopic octahedra does not dissolve in boiling hydrochloric acid, or nitric acid, or nitrohydrochloric acid; but it dissolves in concentrated sulphuric acid, and in fusing bisulphate of potassa.

b. Determination.

Cobalt is determined in the metallic state or as sulphate, being usually first precipitated as hydrated protoxide, sulphide or nitrite of sesquioxide of cobalt and potassa. Cobalt may also be determined volumetrically.

We may convert into

1. Metallic cobalt:

a. By direct reduction. All salts of cobalt, which can be immediately reduced by hydrogen (chloride, nitrate, carbonate, &c.).

b. By precipitation as hydrated protoxide. All salts soluble in water with inorganic acids, and insoluble salts whose acid may be removed by solution. All salts with volatile organic acids.

c. By precipitation as sulphide. All compounds of cobalt without exception.

d. By precipitation as nitrite of sesquioxide of cobalt and potassa. All compounds of cobalt soluble in water or dilute acetic acid.

2. Sulphate of cobalt:

a. By simple evaporation and ignition.—The oxygen compounds of cobalt and all the salts, whose acids may be completely expelled by evaporation and ignition with sulphuric acid.

b. By precipitation as sulphide.—All compounds of cobalt without exception.

The method 1, *a*, is preferable to all others when it can be applied; it is quick and gives exact results. The method 1, *b*, gives better results than it used to be credited with. The direct conversion of suitable cobalt compounds into sulphate is also quite satisfactory. The precipitations as sulphide and as nitrite of sesquioxide of cobalt and potassa are rarely used except in separations. The volumetric methods are more adapted for technical than for scientific purposes.

1. *Estimation as metallic Cobalt.*

a. By direct reduction.

Evaporate the solution of chloride, or nitrate of cobalt (which must be free from sulphuric acid and alkali), in a weighed crucible, to dryness, cover the crucible with a lid having a small aperture in the middle, conduct through this a moderate current of pure dry hydrogen, and then apply a gentle heat, which is to be increased gradually to intense redness. When the reduction is considered complete, allow to cool in the current of hydrogen, and weigh; ignite again in the same way and repeat the process until the weight remains constant. The results are accurate. For the properties of cobalt, see § 80.

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* His Lehrbuch der Titrirmethode.

† Zeitschr. f. anal. Chem. 7, 259.

As regards the apparatus to be employed, see § 108, 2.

b. By precipitation as hydrated protoxide.

The best material for the precipitating vessel is platinum, porcelain may also be used, but not glass. First remove any large excess of acid which may be present by evaporation. Heat nearly to boiling, add pure potash in slight excess, and continue heating till the precipitate is brownish-black. Pour the supernatant fluid through a filter, wash the precipitate by decantation with boiling water repeatedly, transfer it to the filter, and continue the washing with boiling water till the washings are free from any trace of dissolved substance. Dry, ignite in a porcelain crucible (§ 52) till the filter is thoroughly burnt, reduce in a current of hydrogen, wash the metal several times with boiling water, dry, ignite again in hydrogen and weigh. Test the weighed cobalt by dissolving in nitric acid. If any silica remains, this must be weighed and deducted. Mix the solution with chloride of ammonium and carbonate of ammonia, if a small precipitate (alumina or a trace of sesquioxide of iron) forms, weigh this too and deduct it. The results are excellent; the amount of alkali which remains with the metal when the work is done properly being exceedingly minute. Compare § 80, *a*.

c. By precipitation as sulphide.

Put the solution in a flask, add chloride of ammonium, then ammonia just in excess, then sulphide of ammonium as long as a precipitate is produced, fill up to the neck with water, cork and allow to stand 12 or 24 hours in a warm place. Decant, filter, and wash as directed § 109, 2. Finally, dry and proceed as directed § 110, *b*, *a*, to redissolve the cobalt. Determine the cobalt according to *b*. There are no sources of error in the precipitation with sulphide of ammonium. For the properties of the sulphide of cobalt, see § 80. It cannot be brought into a weighable form by ignition in hydrogen, as the residue is a variable mixture of different sulphides (H. Rose). Cobalt may also be thrown down as sulphide by the other methods given under *Nickel*. The thorough precipitation of cobalt is much easier than that of nickel.

d. By precipitation as nitrite of sesquioxide of cobalt and potassa.

To the moderately concentrated solution of the cobalt salt add potash in excess, then acetic acid till the precipitate is just redissolved, then a concentrated solution of nitrite of potash previously just acidified with acetic acid, and allow to stand 24 hours at a gentle heat. Filter, wash with solution of acetate of potash (1 in 10) containing some nitrite of potash, till all foreign substances are removed, dry, dissolve with the filter ash in hydrochloric acid, filter and determine the cobalt according to 1, *b*. This method was introduced by A. Stromeyer;[*] the present modification, first suggested by H. Rose, and improved by Fr. Gauhe, is the surest to yield good results (GAUHE*). For the properties of the precipitate, see § 80, *e*.

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[*] Annal. d. Chem. u. Pharm. 96, 218.

2. *Estimation as sulphate.*

a. By direct conversion.

If the solution contains a volatile acid, add a slight excess of sulphuric acid. Evaporate, using a platinum dish or platinum crucible, at all events, to finish the operation. Heat the residue cautiously over the lamp, gradually increasing the temperature to dull redness, and maintain at this point for 15 minutes. Should the edges blacken, moisten with dilute sulphuric acid, dry, and ignite again with greater caution. Properties of the precipitate, § 80. Results quite satisfactory.†

b. With previous precipitation as sulphide.

Precipitate the cobalt as sulphide according to 1, *c*, dissolve it as directed, evaporate with excess of sulphuric acid in a porcelain dish to dryness, take up the residue with water, transfer the solution to a weighed platinum dish and proceed according to 2, *a*.

3. *Volumetric Methods of estimating Cobalt.*

1. After CL. WINKLER.‡

Principle.—If a solution of chloride of cobalt is mixed with finely divided oxide of mercury shaken up with water (§ 60, 4), no decomposition takes place, and no oxide of cobalt is thrown down; but if now a solution of permanganate of potassa is added, hydrated binoxide of manganese and hydrated sesquioxide of cobalt are precipitated ($6CoCl + 5HgO + 11HO + KO,Mn_2O_7 = 3[Co_2O_3,3HO] + 2[MnO_2,HO] + 5HgCl + KCl$). This equation, however, does not exactly express the change which occurs, as a constant proportion of hydrated protoxide of cobalt falls down with the sesquioxide; or it may be that the cobalt precipitate is a definite compound intermediate between the sesquioxide and the protoxide. Hence the permanganate of potassa must be standardized with cobalt solution, and not with protoxide of iron, or oxalic acid.

Execution.—Dissolve from ·1 to ·2 grm. pure metallic cobalt§ in warm hydrochloric acid, transfer to a 300 c.c. stoppered bottle, dilute to 200 c.c., add excess of oxide of mercury shaken up with water, and then, the fluid being cold, titrate with permanganate of potassa (5 or 6 grm. *pure* salt in 1 litre), shaking constantly, till the fluid in which the brown precipitate is suspended remains red. At first it is hard to see the color of the fluid, towards the end the precipitate settles better, and the color is distinct enough. Addition of more oxide of mercury helps the precipitate to deposit. The color gradually goes away on long standing, which must not be forgotten. The c.c. of permanganate used correspond to the cobalt weighed off. In applying the process to the estimation of unknown quantities of cobalt, proceed in the same way, and let the conditions as regards amount of cobalt, amount of oxide of mercury, and dilution be as nearly as possible the same.

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* Zeitschr. f. anal. Chem. 4, 60.

† Compare GAUHE, Zeitschr. f. anal. Chem. 4, 55.

‡ Zeitschr. f. anal. Chem. 3, 265; 3, 420; 7, 48.

§ WINKLER prepares this as follows. Fill a porcelain crucible one-third with purpureo-cobaltic chloride which has been several times recrystallized and is free from nickel, place this in a large platinum crucible with perforated lid and conducting tube, ignite in a current of hydrogen at first gently till the chloride of ammonium is mostly expelled, then increase the heat finally to the highest point, till no more hydrochloric acid escapes, and allow to cool in the current of gas.

In the presence of sulphuric acid, phosphoric acid, arsenic acid, oxygen acids of nitrogen, or chlorine or organic acids, the method is useless unless modified. Sesquichloride of iron, however, has no injurious action, as the oxide of mercury immediately precipitates all the iron.

The influence of sulphuric acid may always be destroyed by chloride of barium; of phosphoric acid and arsenic acid, when present in moderate quantity, by adding sesquichloride of iron before the oxide of mercury. If one part of sesquioxide of iron is added for one part of arsenic or phosphoric acid, the latter is precipitated as a basic salt. Neither this nor the sulphate of baryta requires to be filtered off.

The presence of manganese renders the method useless. Small quantities of nickel do no damage, large quantities are injurious; see § 160 (Separation of cobalt and nickel). The results are thoroughly satisfactory for technical purposes.

2. In regard to other methods, see *Nickel*—as all the methods there given may be used for cobalt. FLEISCHER's method will be also mentioned under the Separation of cobalt and nickel (§ 160).

5. PROTOXIDE OF IRON.

a. Solution.

Many of the compounds of protoxide of iron are soluble in water. The compounds insoluble in water dissolve almost without exception in hydrochloric acid, in which the pure protoxide also is soluble; the solutions; if not prepared with perfect exclusion of air, and with solvents absolutely free from air, contain invariably more or less sesquichloride. In cases where it is wished to avoid the chance of oxidation, the solution of the compound of protoxide of iron is effected in a small flask, through which a slow current of carbonic acid gas is passed, the transmission of the gas being continued until the solution is cold. Many native proto-compounds of iron cannot be thus dissolved. They are, indeed, rendered soluble by fusing with carbonate of soda, but in this process the protoxide of iron is converted for the most part into sesquioxide. It is therefore advisable to heat such substances (in the finest powder) with a mixture of 3 parts concentrated sulphuric acid and 1 part water in a strong sealed tube of Bohemian glass for 2 hours at about 210°, or—in the case of silicates—to warm them with a mixture of 2 parts hydrochloric acid and 1 part strong hydrofluoric acid in a covered platinum dish (A. MITSCHERLICH*). It is well to cover the water bath on which the dish is heated with a plaster ring about ·1 metre high, to place on this a plaster plate with a piece cut out of the edge, and to conduct carbonic acid through the latter that the solution may take place in an atmosphere which will not oxidize the iron.† Metallic iron dissolves in hydrochloric acid, and dilute sulphuric acid, with evolution of hydrogen, as protochloride or sulphate of protoxide respectively; in warm nitric acid it dissolves as nitrate of sesquioxide, and in nitrohydrochloric acid as sesquichloride.

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* Journ. f. prakt. Chem. 81, 116.

† Somewhat more complicated arrangements for the attainment of the same object are given by COOKE (Zeitschr. f. anal. Chem. 7, 98) and WILBUR and WHITTLESEY (*Ib.* 10, 98).

b. Determination.

Protoxide of iron may be estimated 1, by dissolving, converting into sesquioxide and determining the latter gravimetrically or volumetrically; 2, by precipitating as sulphide, and weighing it as such, or determining it after conversion into sesquioxide; 3, by a direct volumetric method; 4, by treating with terchloride of gold, and weighing the reduced gold.

The methods 1 and 2 are, of course, only applicable when no sesquioxide is present with the protoxide, the method 2 is scarcely ever used except for separations. The methods included under 3 are adapted to most cases and, in absence of other reducing substances, are especially worthy of recommendation. The method 4 will be briefly treated of in the supplement to §§ 112 and 113.

As the determination of iron as sesquioxide belongs to § 113, and as the process for precipitating the protoxide as sulphide is the same as that for precipitating the sesquioxide in this form, nothing remains for us here but to describe the methods of converting the protoxide into the sesquioxide and the processes included under 3.

1. *Methods of converting Protoxide of Iron into Sesquioxide.*

a. Methods applicable in all cases.

Heat the solution of protoxide of iron with hydrochloric acid and add small portions of chlorate of potassa, till the fluid, even after warming for some time, still smells strongly of chlorine. Our object may be also attained by passing chlorine gas or, in the case of small quantities, by addition of chlorine water, or very conveniently by the addition of bromine dissolved in hydrochloric acid. If the solution is required to be free from excess of chlorine or bromine it is finally heated, till all odor of the chlorine or bromine has disappeared.

b. Methods which are only suitable when the iron is to be subsequently precipitated by ammonia, as hydrated sesquioxide.

Mix the solution of the protoxide of iron in a flask with a little hydrochloric acid, if it does not already contain any; add some nitric acid, and heat the mixture for some time to incipient ebullition. The color of the fluid will show whether the nitric acid has been added in sufficient quantity. Though an excess of nitric acid does no harm, still it is better to avoid adding too much on account of the subsequent precipitation. In concentrated solutions, the addition of nitric acid produces a dark-brown color, which disappears upon heating. This color is owing to the nitric oxide formed dissolving in the still unoxidized portion of the solution of the protoxide.

c. Methods which can be employed only when the sesquioxide of iron is to be determined volumetrically.

Add to the hydrochloric solution small quantities of artificially prepared iron-free binoxide of manganese, till the solution is of a dark olive-green color from the formation of sesquichloride of manganese; boil till this coloration and the odor of chlorine have disappeared

(FR. MOHR); or you may add pure permanganate of potassa (in crystals or concentrated solution) till the fluid is just red, and then boil, till the red color and chlorine-odor have vanished. These methods present the advantage of permitting complete oxidation without the use of any considerable excess of the oxidizing agent.

2. *Estimation by Volumetric Analysis.*

a. MARGUERITE'S *Method.*

If we add to a solution of protoxide of iron, containing an excess of sulphuric acid, permanganate of potassa, the former is oxidized, at the expense of the latter, [$10(FeO,SO_3) + 8SO_3 + KO,Mn_2O_7 = 5(Fe_2O_3,3SO_3) + KO,SO_3 + 2(MnO,SO_3)$]. Now if we possess a solution of permanganate of potassa, and know how much iron 100 c.c. of it can convert from the condition of protoxide to that of sesquioxide, we can, with this, readily determine an unknown quantity of iron; we have simply, for this purpose, to dissolve the iron in acid, in the form of protoxide, to oxidize the solution accurately, and note how many c.c. of the solution of permanganate of potassa have been used to accomplish that object.

In the presence of hydrochloric acid the change is not exactly in accordance with the above equation (LÖWENTHAL and LENSSEN*). It is true that by proceeding in a certain way (see γ), we may reduce the error, but the results must always be regarded as less trustworthy.

a. Titration of the Solution of Permanganate of Potassa.

Dissolve 5 grm. (roughly weighed) of pure crystallized permanganate of potassa in distilled water by the aid of heat, dilute to 1 litre, and preserve in a stoppered bottle. Action of direct sunlight on the solution should be avoided. The solution, if carefully kept, does not alter, but still it is well to titrate it afresh occasionally.

aa. Titration by Metallic Iron.

Weigh off accurately about 1 grm. thin soft iron wire, previously cleaned with emery paper, transfer to a ¼ litre measuring flask, containing 100 c.c. dilute sulphuric acid (1 to 5), add about 1 grm. bicarbonate of soda, to produce carbonic acid and expel the air, and then close the flask with an india-rubber stopper, provided with an evolution tube, as shown in fig. 80; *c* contains 20 or 30 c.c. water. Heat the flask at first gently, finally to gentle boiling till the iron is dissolved. The clip *b* is open, and the hydrogen escapes through the water in *c*. Meanwhile boil about 300 c.c. distilled water, to drive out all the air it contains, and then allow it to cool. As soon as the iron is entirely dissolved, remove the lamp and close the evolution tube with the clip. When the iron solution has cooled a little loose the clip, and allow the water in *c* to recede, pour the boiled water into *c*, and allow this also to recede till the solution nearly reaches the mark. Take out the evolution tube and close the flask with an unperforated stopper, allow to cool to the temperature of the room, fill with water to the mark, shake and allow to stand, so that the particles of carbon usually present may deposit. Now take out with a pipette 50 c.c. of the clear and nearly colorless fluid (containing ⅕ of the iron weighed off), transfer to a 400 c.c. beaker, and dilute till the beaker is half full. Place the beaker on a sheet of white paper, or better, on a sheet of glass, with white paper underneath.

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* Zeitschr. f. anal. Chem. 1, 329.

Fill a GAY-LUSSAC's or GEISSLER's burette of 30 c.c. capacity, divided into $\frac{1}{10}$ c.c. (see § 22, figs. 23 and 24), up to zero, with solution of permanganate of potassa, of which take care to have ready a sufficient quantity, perfectly clear and uniformly mixed.

Now add the permanganate to the iron solution, stirring the latter all the while with a glass rod. At first the red drops disappear very rapidly, then more slowly. The fluid, which at first was nearly colorless, gradually acquires a yellowish tint. From the instant the red drops begin to disappear more slowly, add the permanganate with more caution and in single drops, until the last drop imparts to the fluid a faint, but unmistakable reddish color, which remains on stirring. A little practice will enable you readily to hit the right point. As soon as the fluid in the burette has sufficiently collected again read off, and mark the number of c.c. used. The reading off must be performed with the greatest exactness (see § 22); the whole error should not amount to $\frac{1}{10}$ c.c.

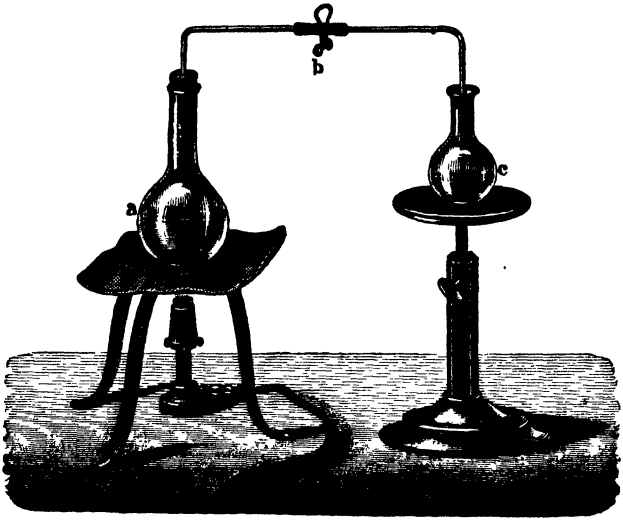

Fig. 80.

The amount of permanganate solution used should be about 20 c.c. Repeat the experiment with another 50 c.c. of the iron solution. The difference between the permanganate used in the two cases should not be more than ·1 c.c.; if it is, make one more experiment and when the results are sufficiently near take the mean. Now calculate what quantity of iron is represented by 100 c.c. of the permanganate. To this end first divide the iron weighed off by 5, and then multiply by ·996, since soft iron wire contains on the average ·4 per cent. carbon, &c.; this gives the quantity of pure iron contained in 50 c.c. of the solution. Suppose we took 1·050 grm. iron wire, and used a mean of 21·3 c.c. permanganate, $\frac{1\cdot050}{5} = \cdot210$, $\cdot210 \times \cdot996 = \cdot20916$. And then by rule of three:—

$$21\cdot3 : \cdot20916 :: 100 : x \text{——} x = \cdot98197;$$

therefore, 100 c.c. permanganate = ·98197 pure iron.

If there is a deficiency of free acid in the solution of iron, the fluid acquires a brown color, turns turbid, and deposits a brown precipitate (binoxide of manganese and sesquioxide of iron). The same may happen also if the solution of permanganate of potassa is added too quickly, or if the proper stirring of the iron solution is omitted or interrupted. Experiments attended with abnormal manifestations of the kind had always better be rejected. That the fluid reddened by the last drop of solution of permanganate of potassa added, loses its color again after a time, need create no surprise or uneasiness; this decolorization is, in fact, quite inevitable, as a dilute solution of free permanganic acid cannot keep long undecomposed.

bb. Titration by Sulphate of Iron and Ammonia.

Weigh off, with the greatest accuracy, about 1·4 grm. of the pure salt prepared according to the directions given in § 65, 4, dissolve in about 200 c.c. distilled water, previously mixed with about 20 c.c. dilute sulphuric acid, and proceed as in *aa.*

By dividing the amount of salt weighed off by 7·0014 (or where great accuracy is not required by 7) we obtain the quantity of iron corresponding.

If the salt is not pure, if, for instance, it contains bases isomorphous with protoxide of iron (protoxide of manganese, magnesia, &c.); or if it contains sesquioxide, or is moist, the result will of course be too high.

cc. Titration by Oxalic Acid.

If solution of permanganate of potassa is added to a warm solution of oxalic acid, mixed with sulphuric acid, the liberated permanganic acid instantly oxidizes the oxalic acid to carbonic acid [$5C_2O_3 + 3SO_3 + KO,Mn_2O_7 = 10CO_2 + 2(MnO,SO_3) + KO,SO_3$.] For the oxidation of 1 eq. oxalic acid (C_2O_3) and 2 eq. iron (in the state of protoxide) equal quantities of permanganic acid are accordingly required; therefore, 63 parts (1 eq.) of crystallized oxalic acid correspond, in reference to the oxidizing action of permanganic acid, to 56 parts (2 eq.) of iron.

A solution of oxalic acid is altered by the action of light; it is, therefore, well only to dissolve as much as will be required for immediate use. Dissolve 1 to 1·2 grm. pure acid prepared by § 65, 1, to 250 c.c.; 50 c.c. of this solution are introduced into a beaker, diluted with about 100 c.c. water, from 6 to 8 c.c. conc. sulphuric acid added, and the fluid heated to about 60°. The beaker is then placed on a sheet of white paper, and permanganate added from the burette, with stirring. The red drops do not disappear at first very rapidly, but when once the reaction has fairly set in, they continue for some time to vanish instantaneously. As soon as the red drops begin to disappear more slowly, the solution of permanganate of potassa must be added with great caution; if proper care is taken in this respect, it is easy to complete the reaction with a single drop of permanganate; this completion of the reaction is indicated with beautiful distinctness in the colorless fluid. To find the iron corresponding to the permanganate used, multiply the amount of crystallized oxalic acid in the 50 c.c. by 8 and divide by 9.

If the oxalic acid was not perfectly dry, or not quite pure, the result of the experiment will, of course, lead to fixing the strength of the solution of permanganate of potassa too high. Instead of pure oxalic acid, SAINT-GILLES has proposed to use crystallized oxalate of ammonia ($NH_4O,C_2O_3 + aq.$) This can easily be prepared in the pure state, keeps well, and can be weighed with accuracy. 71·04 parts of the crystallized salt correspond to 56 parts iron.

Of the foregoing three methods of standardizing solution of permanganate of potassa, the first is the one originally proposed by MARGUERITE. Sulphate of iron and ammonia was first proposed by FR. MOHR, and oxalic acid by HEMPEL, as agents suitable for the purpose. With absolutely pure and thoroughly dry reagents, and proper attention, all three methods give correct results.

For myself, I prefer the first method, as the most direct and positive, the only doubtful point about it being the question whether the assumption that the iron wire contains 99·6 per cent. of chemically pure iron is quite correct; this, however, is of very trifling importance, as the error could not exceed $\frac{1}{10}$ or $\frac{2}{10}$ per cent.* The other two methods are, as may readily be seen, somewhat more convenient, but they are not so trustworthy unless you can insure the purity and dryness of the preparations.

For the analysis of very dilute solutions of iron, *e.g.*, chalybeate water, in which the amount of iron may be very approximately determined with great expedition, by direct oxidization with permanganate, a very dilute standard solution must be prepared. Such a solution may be made by diluting the previous solution with 9 parts of water or by dissolving ·5 grm. crystals of permanganate of potassa in 1 litre of water. It is to be directly standardized with correspondingly small quantities of iron, iron salt, or oxalic acid.

In experiments of this kind, the fact that a certain quantity of permanganate is required to impart a distinct color to pure acidified water (which is of no consequence in operations where the concentrated solution is used) must be taken into consideration; for where the solution used is so highly dilute, it takes indeed a measurable quantity of it to impart the desired reddish tint to the amount of water employed. In such cases, the volume of the solution of iron used for standardizing the permanganate and the volume of the weak ferruginous solution subjected to analysis should be the same, and either the two solutions should contain about the same quantity of iron, or by means of a special experiment, it is ascertained how many $\frac{1}{10}$ c.c. of the permanganate are required to impart the desired pale red color to the same volume of acidified water. In the latter case, these $\frac{1}{10}$ c.c. will be deducted from the amount of permanganate used in the regular experiments. In estimating the iron in mineral waters it is of course taken for granted that the water contains no other substance which will deoxidize the permanganate such as sulphuretted hydrogen, organic matter, and nitrous acid, compare § 208.

β. Performance of the Analytical Process.

This has been fully indicated in *a*. The compound to be examined is dissolved, preferably with application of a current of carbonic acid (see fig. 81), in dilute sulphuric acid, allowed to cool in the current of carbonic acid, and suitably diluted (if practicable, the solution of a substance containing about ·2 grm. iron should be diluted to about 200 c.c.); if free acid is not present in sufficient quantity, dilute sulphuric acid is added till about 20 c.c. are present altogether, and then standard permanganate from the burette, to incipient reddening of the fluid. The volume of standard solution used is then read off. The strength of the solution of permanganate being known, the quantity of iron present in the examined fluid is found by a very simple calculation. Suppose 100 c.c. of solution of permanganate of potassa to correspond to ·98 grm. iron, and 25 c.c. of the solution to have been used to effect the oxidation of the protoxide of iron in the examined compound, then

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* If you are often making iron determinations, you may of course procure a quantity of wire and estimate the foreign matter in it.

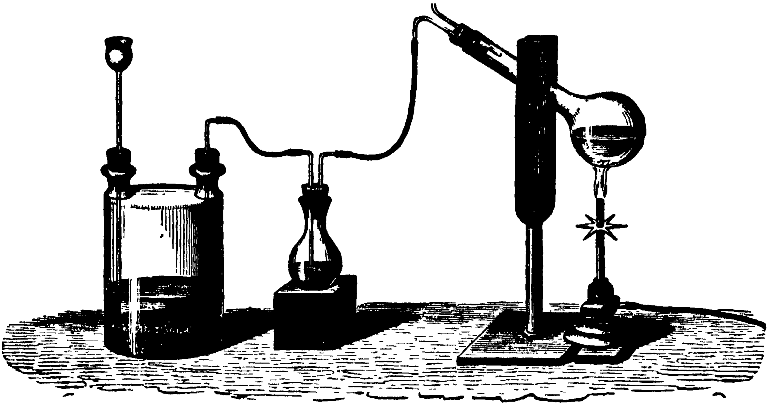

Fig. 81.

$$100 : 25 :: \cdot 98 : x; \quad x = \cdot 245.$$

The quantity of iron originally present in the form of protoxide amounted accordingly to ·245 grm.

For the method of determining the total amount of iron present in a solution containing both protoxide and sesquioxide of that metal, I refer to § 113; for that of determining the amount of each separately, to Section V.

γ. Process to be used with hydrochloric solutions of Iron.

In titrating hydrochloric acid solutions of iron with permanganate, it is essential that the standardizing of the reagent and the actual analysis be performed under the same circumstances as regards dilution, amount of acid, and temperature. Besides the proper reaction $10\,FeO + Mn_2O_7 = 5Fe_2O_3 + 2MnO$, the collateral reaction $7HCl + Mn_2O_7 = 5Cl + 2MnCl + 7HO$ also takes place, in consequence of which a little chlorine is liberated. This chlorine does not oxidize the protoxide of iron in the case of considerable dilution, but there occurs a condition of equilibrium in the fluid containing protoxide of iron, chlorine, and hydrochloric acid, which is destroyed by addition of a further quantity of either body (LÖWENTHAL and LENSSEN*). But since it is difficult to observe the above conditions of obtaining correct results, the estimation of hydrochloric acid solutions of iron is always less trustworthy than the estimation of sulphuric acid solutions.

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* Zeitschr. f. anal. Chem. 1, 329.

The following method I have, however, found* to give the best results:—

Standardize the permanganate by means of iron dissolved in dilute sulphuric acid, make the iron solution to be tested up to ¼ litre, add 50 c.c. to a large quantity of water acidified with sulphuric acid (about 1 litre), titrate with permanganate, then again add 50 c.c. of the iron solution, and titrate again, &c. &c. The numbers obtained at the third and fourth time are taken. These are constant, while the number obtained the first time, and sometimes also the second time, differs. The result multiplied by 5 gives exactly the quantity of permanganate proportional to the amount of protoxide of iron present.

b. PENNY's *Method* (recommended subsequently by SCHABUS).

If bichromate of potassa is added to a strongly acid solution of protoxide of iron, the latter is converted into sesquioxide, whilst the chromic acid is reduced to sesquioxide of chromium ($6FeO + 2CrO_3 = 3Fe_2O_3 +$

Now, with ·1 eq. bichromate of potassa = 14·761 grm. dissolved to 1 litre of fluid, ·6 eq. = 16·8 grm. iron may be converted from the state of protoxide to that of sesquioxide, and 50 c.c. of the above solution correspond accordingly to ·84 grm. iron.

Care must be taken to use perfectly pure bichromate of potassa; the salt is heated in a porcelain crucible until it is just fused; it is then allowed to cool under the desiccator, and the required quantity weighed off when cold. Besides the above solution, another should also be prepared, ten times more dilute, and containing accordingly ·01 eq. of bichromate of potassa in the litre.

It is always advisable to test the correctness of the standard solution of bichromate of potassa, by oxidizing with it a known amount of pure iron dissolved to protoxide (see p. 215, *aa*).

The solution of protoxide of iron is sufficiently diluted, mixed with a sufficient quantity of dilute sulphuric acid, and the standard solution of bichromate of potassa slowly added from the burette, the liquid being stirred all the while with a thin glass rod. The fluid, which is at first nearly colorless, speedily acquires a pale green tint, which changes gradually to a darker chrome-green. A very small drop of the mixture is now from time to time taken out by means of the stirring-rod, and brought into contact with a drop of a solution of ferricyanide of potassium (free from ferrocyanide) on a porcelain plate, which has been spotted with several of such drops. When the blue color thereby produced begins to lose the intensity which it exhibited on the first trials, and to assume a paler tint, the addition of the solution of bichromate of potassa must be more carefully regulated than at first, and towards the end of the process, a fresh essay must be made, and with larger drops than at first, after each new addition of two drops, and finally, even of a single drop; drops must also be left for some time in contact before the observation is taken. When no further blue coloration ensues, the oxidation is terminated. From the remarkable sensitiveness of the reaction, the exact point may be easily hit to a drop. To heighten the accuracy of the results, the dilute (ten times weaker) standard fluid should, just at the end of the process, be substituted for the concentrated solution of bichromate of potassa. It is also well to make the iron solution up to 250 c.c., and to take 50 c.c. at first to make a rough determination, and then another 50 c.c. for the determination proper; in this way the loss of substance inherent in the method is reduced to a minimum.

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* Zeitschr. f. anal. Chem. 1, 361.

If exactly ·84 grm. of the substance to be analysed has been dissolved, the numbers of half c.c. used of the two standard fluids show how many per-cents., and tenths per cent. respectively of pure iron the analysed substance contains in the form of protoxide. For the manner of proceeding in presence of sesquioxide of iron, I refer to § 113. If there is a deficiency of free acid in the solution, brown chromate of sesquioxide of chromium may form, upon which the solution of protoxide of iron exercises no longer a deoxidizing action.

The advantage of the first of these two volumetric methods is, that the end of the operation is at once evident by the coloration of the fluid without any special testing; the advantage of the second is, that the standard solution may easily be prepared and preserved unaltered. Since it has been known that the results yielded by the former method in hydrochloric solutions are not free from suspicion, the latter method, which has been for some time neglected, has come again into use.

Wherever in making a volumetric estimation you are free to choose between a hydrochloric and a sulphuric acid solution, preference should be given to the latter, since it is less likely to absorb oxygen from the air (PATTINSON*).

§ 113.

6. SESQUIOXIDE OF IRON.

a. Solution.

Many of the compounds of sesquioxide of iron are soluble in water. Pure sesquioxide of iron and most of those of its compounds which are insoluble in water, dissolve in hydrochloric acid, but many of them only slowly and with difficulty; compounds of this nature are best dissolved in concentrated hydrochloric acid, in a flask, with the aid of heat; which, however, should not be allowed to reach the boiling point; the compound must, moreover, be finely powdered, and even then it will often take many hours to effect complete solution. Sometimes the compound (strongly ignited sesquioxide, for instance) is dissolved in fusing bisulphate of potash, or a mixture of 8 parts sulphuric acid and 3 parts water. It is frequently worth while to reduce the sesquioxide to metallic iron by prolonged ignition in hydrogen, and then to dissolve the metal. Silicates undecomposable by hydrochloric acid are treated according to § 140, *b*.

b. Determination.

Sesquioxide of iron is usually weighed as such, but sometimes as sulphide (§ 81). It may, however, be estimated also indirectly, and also by volumetric analysis, both directly and after reduction to protoxide. The conversion of compounds of iron into sesquioxide is effected either by precipitation as hydrated sesquioxide, preceded in some cases by precipitation as sulphide of iron, or as highly basic sesquichloride or basic acetate or basic formate of sesquioxide of iron; or it is effected by ignition. While the volumetric and the now seldom-used indirect methods are applicable in almost all cases, we may convert into

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* Zeitschr. f. anal. Chem. 9, 512.

1. SESQUIOXIDE OF IRON:

a. By Precipitation as hydrated sesquioxide. All salts soluble in water with inorganic or volatile organic acids and likewise those which, insoluble in water, dissolve in acids, with separation of their acid.

b. By Precipitation as sulphide of iron. All compounds of iron without exception.

c. By Ignition. All salts of sesquioxide of iron with volatile oxygen acids.

2. SULPHIDE OF IRON: All compounds of iron without exception.

The method 1, *c*, is the most expeditious and accurate, and is therefore preferred in all cases where its application is admissible. The method 1, *a*, is the most generally used. The methods, 1, *b*, and 2, serve principally to effect the separation of the sesquioxide of iron from other bases; they are resorted to also in certain instances where *a* is inapplicable, especially in cases where sugar or other non-volatile organic substances are present; and also to estimate the sesquioxide of iron in its compounds with phosphoric acid and boracic acid. For the manner of determining the sesquioxide of iron in the chromate and silicate, I refer to §§ 130 and 140. The volumetric methods for estimating the sesquioxide are used in technical experiments almost to the exclusion of all others, and are very frequently employed in scientific analyses. The methods of precipitating the iron as basic salts will be given in Section V.

1. *Determination as Sesquioxide of Iron.*

a. By Precipitation as Hydrated Sesquioxide.

A porcelain dish should be used, a beaker does not answer the purpose so well. Mix the solution with ammonia in excess, heat nearly to boiling, decant repeatedly on to a filter, wash the precipitate carefully with hot water, dry thoroughly (which very greatly reduces the bulk of the precipitate), and ignite in the manner directed in § 53.

For the properties of the precipitate and residue, see § 81. The method is free from sources of error. The precipitate, under all circumstances, even if there are no fixed bodies to be washed out, must be most thoroughly washed, since, should it retain any traces of chloride of ammonium, a portion of the iron would volatilize in the form of sesquichloride. It is also highly advisable to dissolve the weighed residue, or a portion of it, in strong hydrochloric acid, or to fuse it with bisulphate of potash, and treat the fusion with dilute hydrochloric acid to see whether the oxide is quite free from silica. The easiest way, however, to test it is to reduce it to metal by ignition in hydrogen, and then to dissolve in dilute hydrochloric acid.

b. By Precipitation as Sulphide of Iron.

The solution, in a not too large flask, is mixed with ammonia till all the free acid is neutralized. (In the absence of organic non-volatile substances this leads to the precipitation of a little hydrated sesquioxide, which, however, is of no consequence.) Add chloride of ammonium, if not already present in sufficient quantity, then colorless or yellowish sulphide of ammonium in moderate excess, lastly water, till the fluid reaches to the neck of the flask. Cork it up and stand in a warm place, till the precipitate has subsided, and the supernatant fluid has a clear yellowish appearance (without a tinge of green). Wash the precipitate, if at all considerable, by decantation and finally on the filter, using water containing sulphide of ammonium, and gradually decreasing quantities of chloride of ammonium. While decanting pour the fluids in a flask, and when all the decantations are over filter the fluids; then transfer the precipitate to the filter and continue the washing uninterruptedly, keeping the funnel covered with a glass plate. Neglect of any of these precautions will occasion some loss of substance, the sulphide of iron gradually combining with the oxygen of the air, and passing thus into the filtrate as protosulphate. As this sulphate is reprecipitated by the sulphide of ammonium present, the filtrate assumes, in such cases, a greenish color, and gradually deposits a black precipitate, the separation of which is much promoted by addition of chloride of ammonium.

When the operation of washing is completed, the moist precipitate (if it is not dried and determined according to 2) is put, together with the filter, into a beaker, some water added, and then hydrochloric acid, until the whole is redissolved. Heat is now applied, until the solution smells no longer of sulphuretted hydrogen; the fluid is then filtered into a flask, the residual paper carefully washed and then incinerated, the ash is warmed with strong hydrochloric acid, the solution (if it looks yellow) diluted and filtered to the principal solution, which is now oxidized by heating with nitric acid (see § 112, 1); the oxidized solution is finally precipitated with ammonia, as in *a*.

If a solution of potassio-, sodio-, or ammonio-tartrate of sesquioxide of iron contains a considerable excess of alkaline carbonate, the precipitation of the iron as sulphide is prevented to a greater or less extent (BLUMENAU). In such cases the fluid must therefore be nearly neutralized with an acid, before the precipitation with the sulphide of ammonium can be effected.

c. By Ignition.

Expose the compound, in a covered crucible, to a gentle heat at first, and gradually to the highest degree of intensity; continue the operation until the weight of the residuary sesquioxide of iron remains constant.

2. *Determination as Anhydrous Sulphide of Iron.*

The hydrated sulphide of iron obtained, as in 1, *b*, may be very conveniently determined by conversion into the anhydrous sulphide. The process is the same as for zinc (§ 108, 2). The heat to which it is finally exposed in the current of hydrogen must be strong enough, as an excess of sulphur is retained with some obstinacy. In fact, it is advisable after weighing to re-ignite in hydrogen and weigh a second time. It is of no importance if the hydrated sulphide has oxidized on drying. Protosulphate and sesquioxide of iron can be transformed into sulphide in the same manner, after having been dehydrated by ignition in a porcelain crucible (H. **Rose**[*]). The results obtained by **Oesten**, and adduced by **Rose**, as well as those obtained in my own laboratory, are exceedingly satisfactory (Expt. No. 67).

3. *Determination by Volumetric Analysis.*

a. Preceded by Reduction of the Sesquioxide to Protoxide.

The volumetric methods which come under this head are based upon the reduction of the sesquioxide to protoxide, and the estimation of the latter. We have, accordingly, to occupy ourselves simply with the reduction of the solution of the sesquioxide, the other part of the process having been fully discussed in § 112. The reduction of sesquioxide of iron can be effected by a host of substances (zinc, protochloride of tin, sulphuretted hydrogen, sulphurous acid, &c.), but only those can be used with advantage, an excess of which may be added with impunity. If an excess must be very carefully avoided, or, being added, must be carefully removed, the method becomes troublesome, and a ready source of inaccuracy is introduced. On these grounds, although its action is somewhat slow, zinc, unquestionably, deserves the preference before all other reducing agents.

Heat the hydrochloric or sulphuric acid solution, which must contain a moderate excess of acid, but be free from nitric acid,[†] in a small long-necked flask, placed in a slanting position; drop in small pieces of iron-free zinc (§ 60) with a spiral of platinum wire or a piece of platinum foil, and conduct a slow current of carbonic acid through the flask (fig. 81, p. 219). Evolution of hydrogen gas begins at once, and the color of the solution becomes paler in proportion as the sesquioxide changes to protoxide. Apply a moderate heat to promote the action; and add also, if necessary, a little more zinc. As soon as the hot solution is completely decolorized (one cannot judge of the perfect deoxidation of a cold solution so well, as the color of the sesquichloride or sesquisulphate of iron is deeper in the heat), and the whole of the zinc is dissolved,[‡] allow to cool completely in the stream of carbonic acid; to hasten the cooling the flask may be immersed in cold water; then dilute the contents with water, pour off, and wash carefully into a beaker, leaving behind as far as possible any flocks of lead that may have separated from the zinc, and proceed as directed, p. 218, *β*, if you have a sulphuric acid solution, as directed p. 220, *b*, if hydrochloric acid is present. If the solution contains metals precipitable by zinc, these will separate, and may render filtration necessary. In this case the filtrate must be again heated with zinc, before titrating. If iron-free zinc cannot be procured, the percentage of iron in the metal used must be determined, and weighed portions of it employed in the process of reduction; the known amount of iron contained in the zinc consumed is then subtracted from the total amount of iron found.

☞ In the analysis of solid compounds of sesquioxide of iron, it is advisable to add some zinc while they are dissolving in hydrochloric acid. The solution is thereby facilitated (O. L. **Erdmann**[§]).

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[*] Pogg. Annal. 110, 126.

[†] Nitric acid under the influence of zinc forms nitrous acid, which reduces permanganate of potassa (**Terreil**, Zeitschr. f. anal. Chem. 6, 116).

[‡] Iron often precipitates in the zinc, and does not redissolve till the zinc itself dissolves (A. **Mitscherlich**, Zeitschr. f. anal. Chem. 2, 72).

[§] Journ. f. prakt. Chem. 76, 176.

With respect to the reduction of sesquichloride of iron by means of protochloride of tin, compare *b*.

b. Without Previous Reduction to Protoxide.

The methods under this head all depend on adding a reducing agent to the solution till the sesquioxide is entirely converted into protoxide, and then determining the amount of the reducing agent used either directly or indirectly. Many methods have been proposed, but I have found those given under *α* and *β* the best.

α. Reduction by Protochloride of Tin.[*]

Having had many years' experience with this method, I can most strongly recommend it. We require :

a. A Standard Solution of Sesquichloride of Iron. This is prepared by dissolving 10·04 grm. of clean, fine, and soft iron wire (= 10 grm. pure iron), in hydrochloric acid in a slanting long-necked flask, oxidizing the solution with chlorate of potassa, *completely* removing the excess of chlorine by protracted gentle boiling, and finally diluting the solution to 1 litre.

b. A Clear Solution of Chloride of Tin. It should be of such a strength that one volume may reduce about two volumes of the sesquichloride of iron.

c. A Solution of Iodine in Iodide of Potassium, containing about ·010 grm. iodine in 1 c.c. The quantity of iodine it contains need not be exactly known.

The operations are as follows :—

1. Run 2 c.c. of the chloride of tin into a small beaker, add a little starch solution and 5 c.c. water, then iodine solution from the burette till the fluid is permanently blue. About 5 c.c. iodine will be required for 1 c.c. chloride of tin.[†] Divide the c.c. of chloride of tin by the c.c. of iodine solution, and preserve the fraction obtained.

2. Measure off 50 c.c. of the standard iron solution into a small flask, add some hydrochloric acid, and heat, preferably on an iron plate, to boiling. Now add chloride of tin from the burette, at first in larger, then in smaller quantities, allowing a certain interval between each addition, and keeping gently boiling all the while. The yellow color becomes lighter and lighter as the reduction progresses. Towards the end add the reagent in drops, and allow sufficient time for their action. It is thus easy to hit the point of complete reduction, for the passage of the yellowish solution into the colorless state is readily perceived. Cool the contents of the flask, add some starch-paste, and then iodine from the burette, till blue. The amount of iodine used[‡] is

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[*] PENNY and WALLACE have already made use of the same principle in another way, but I believe I was the first to give the method a practical form (Zeitschr. f. anal. Chem. 1, 26).

[†] The quantity of iodine here used varies a little, according to the quantity of free hydrochloric acid mixed with the chloride of tin. However, the differences are so trifling as to have no appreciable influence on the result, since in the method before us, the excess of chloride of tin that has to be determined is always very slight.

[‡] If the tin solution has been added at last very carefully, especially where the solution of iron is concentrated, it often happens that the excess of chloride of tin is too small to be estimated. But in other cases a small excess will be found to have been added. In order to render the method really reliable, I consider it absolutely necessary to test for an excess of chloride of tin, and, if present, to determine it in the manner described.

then transferred into chloride of tin (by multiplying by the fraction obtained in 1), which is deducted from the whole quantity of chloride of tin used, and the remainder is the amount necessary to convert ·5 grm. of iron from the condition of sesquioxide to that of protoxide.

3. Having thus standardized the protochloride of tin, we may employ it for our purpose as follows: Dissolve the compound of iron in hydrochloric acid, convert any protochloride present into sesquichloride, according to one of the methods given, § 112, 1, *a* or *c*, remove every trace of free chlorine, and lastly, to the sufficiently concentrated solution add the chloride of tin, as described in 2, and determine any excess of the latter. The amount of iron in our substance may then be obtained from the chloride of tin used by a simple rule-of-three sum. Suppose, for instance, 25 c.c. of the tin solution correspond to ·5 grm. of iron (*i.e.*, are capable of converting exactly ·5 grm. iron from sesqui- to protoxide) and 20 c.c. of the tin solution have been used to reduce the unknown quantity of iron,

$$25 : \cdot 5 :: 20 : x; \; x = \cdot 4$$

and the amount of iron in the substance was ·4 grm. The method affords exceedingly satisfactory results.*

But all the operations must be done at once, so as not to leave time for the strength of the tin solution to be altered by the action of the air. It is preferable to use a rather strong solution of tin (and consequently rather large quantities of substance) than to use a very dilute solution of tin, on which the air would have more action.

The tin solution is made as follows:—Melt tin in a porcelain dish, and while cooling rub it with a pestle. Heat the powder so obtained with hydrochloric acid of 1·12 sp. gr. till, the tin being in excess, no more hydrogen is given off. When cold, pour off or filter the solution and add 3 volumes of hydrochloric acid and 6 volumes of water. To keep the solution, it is well to use an arrangement which prevents or as far as possible limits the action of the air.

Formerly† the air entering the bottle containing the tin solution was made to pass through tubes containing phosphorus and pyrogallate of potash, to free it from oxygen; now I prefer the apparatus, fig. 82, especially for large laboratories. The syphon tube, *f*, is filled by blowing air through *b*. The clip, *g*, is then put on, the

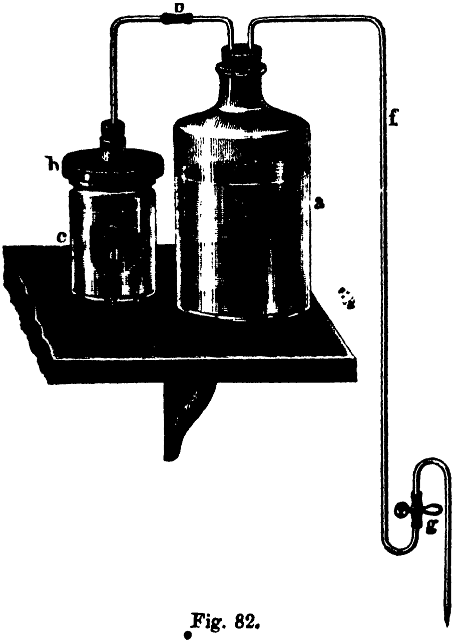

Fig. 82.

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* Zeitschr. f. anal. Chem. 1, 26.

† *Ib.* 2, 58.

constant carbonic acid apparatus, *c*, is connected with *b*, the stopper, *a*, is loosened, and the air in the latter replaced by carbonic acid. When any tin solution is drawn off by loosing the clip, *g*, an equal volume of carbonic acid passes from *c* to *a*, and *g* being closed the evolution of carbonic acid ceases as soon as the acid is pressed out of *d*. *d*, which contains marble, has of course a small opening at the bottom; it is held down by the plaster plate, *h*.

β. Reduction by iodide of potassium, and estimation of the liberated iodine by hyposulphite of soda.[*]

If excess of iodide of potassium acts upon solution of sesquichloride of iron at a certain heat, the following reaction takes place: $Fe_2Cl_3 + KI = 2FeCl + KCl + I$. The iodine remains in solution in the excess of iodide of potassium; it is determined by standard solution of hyposulphite of soda, and gives by calculation the quantity of iron present, since 1 eq. iodine = 126·85 represents 2 eq. iron = 56. The reaction between the iodine and the hyposulphite of soda is $2(NaO,S_2O_2) + I = NaI + NaO,S_4O_5$.

The method requires—1. A solution of hyposulphite of soda containing about 12 grm. of the crystals in the litre. 2. Iodide of potassium free from iodate (§ 65, 6). 3. Solution of sesquichloride of iron of known strength, free from protosalt and free chlorine, compare § 113, *b*, *a*; the solution there described containing ·1 grm. iron in 10 c.c. is very suitable. 4. A few bottles holding 100 to 150 c.c. with closely fitting stoppers. 5. Thin freshly prepared starch paste.

The hyposulphite of soda is titrated as follows. Take two of the bottles and into each measure 10 c.c. of the iron solution. In order that the solution may only be slightly acid, add dilute soda till a few flocks begin to separate and then hydrochloric acid (·5 to 1 c.c. of sp. gr. 1·1) to redissolve them. The solution should not be brownish-red but dark-yellow. Add to each bottle about 3 grm. iodide of potassium, insert the stoppers firmly, fasten them down with moist parchment paper, or wire or string, and warm the bottles to 50° or 60°; this is best done by suspending them over a water bath, so that they may catch the steam. In 15 or 20 minutes the action is complete. Allow to cool and then run in the hyposulphite from the burette till the solution is very pale yellow, add about 1 c.c. of the thin starch, and then again hyposulphite till the blue color is just discharged. The c.c. used correspond to the iodine separated by the agency of ·1 grm. iron, and therefore to ·1 grm. iron present as sesquichloride.

The estimation of iron in a solution of an unknown amount is conducted in the same way as the titration of the hyposulphite of soda. All the iron must be in the state of sesquichloride or sesquioxide, and of course no other substance may be present which might decompose the iodide of potassium, such as free chlorine and nitric acid. It is well to take a quantity of the substance containing not much more or much less than ·1 grm. The free acid present must be nearly neutralized as directed above.

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[*] The method to be described passed through many phases before it arrived at the present state. DUFLOS and afterwards STRENG employed the reduction of sesquichloride of iron by hydriodic acid for estimating iron. In 1858 (Annal. d. Chem. u Pharm. 105, 53) C. MOHR studied the influence of dilution on this reaction. In 1860 FR. MOHR (Annal. d. Chem. u. Pharm. 113, 257) described a mode of proceeding in which the iodide of potassium was not added in excess, and played the part more of an indicator; still the process was not quite satisfactory. In the same year C. D. BRAUN (Journ. f. prakt. Chem. 81, 423) applied the method to estimate the sesquichloride of iron produced by the action of nitric acid on the protochloride, but he improved upon it by using excess of iodide of potassium, aiding the action by heat and determining the separated iodine after cooling. In 1863 FR. MOHR (Zeitschr. f. anal. Chem. 2, 243) described the method, adopting BRAUN's improvements, but titrating the hyposulphite solution by iodine separated by means of bichromate of potassa. In 1864 BRAUN (Zeitschr. f. anal. Chem. 3, 452) described again his method of proceeding in detail.

If it was found that ·1 grm. iron = 18·4 c.c. hyposulphite, and if 24·5 c.c. of the latter were required in an analysis, then the iron present is ·13315 grm., for 18·4 : ·1 :: 24·5 : ·13315.

The method gives good results and is much to be recommended for the estimation of small quantities of iron.

γ. *Reduction by hyposulphite of soda in the presence of a copper salt, after* OUDEMANS.*

If an acid solution of sesquichloride of iron is mixed with a little sulphate of copper and some sulphocyanide of potassium and then hyposulphite of soda is added, the red color of the sesquisulphocyanide of iron gets paler and paler, and finally disappears altogether. Warming is unnecessary. To hit the point is not easy, so we add a slight excess of hyposulphite of soda, and then titrate back with standard iodine. The reaction is as follows: $Fe_2Cl_3 + 2(NaO,S_2O_2) = 2FeCl + NaO,S_4O_5 + NaCl$; it is promoted by the addition of a small quantity of sulphate of copper, which is alternately reduced by the hyposulphite and oxidized by the sesquichloride of iron. If a small quantity of subsalt of copper is produced by the excess of hyposulphite this does not matter, as its action on the iodine solution is the same in extent as the action of the hyposulphite which produced it. The method is not accurate unless the fluid remains clear; neither subsulphocyanide of copper nor subiodide of copper nor sulphur must be thrown down. Hence care must be taken to maintain the proper amounts of the reagents and to dilute the fluid sufficiently.

We require—1. A solution of hyposulphite of soda. 2. A solution of sesquichloride of iron of known strength (see β for these two solutions). 3. A solution of sulphate of copper, 1 in 100. 4. A solution of sulphocyanide of potassium, 1 in 100. 5. A solution of iodine in iodide of potassium, containing 5 or 6 grm. iodine in the litre (compare § 146, 3). 6. Thin starch paste.

Measure off some of the hyposulphite of soda, add starch paste (§ 146, 3), and then titrate with iodine solution, in order to determine the relation between the two solutions. Now transfer 10 or 20 c.c. of the sesquichloride of iron to a beaker, add 2 c.c. concentrated hydrochloric acid, 100 or 150 c.c. water, 3 c.c. copper solution, and 1 c.c. sulphocyanide of potassium, titrate with hyposulphite till the fluid just loses its color, add at once some starch paste, and titrate back with iodine solution till the blue color appears. Deduct the hyposulphite equivalent to the iodine solution from the total quantity of hyposulphite used, and the remainder will represent the iron present.

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* Hyposulphite of soda was first employed by SCHERER (Gel. Anz. der K. Bayerischen Akademie, vom 21 Aug 1859), afterwards by KREMER and LANDOLT (Zeitschr. f. anal. Chem. 1, 214). The method of OUDEMANS is to be found in Zeitschr. f. anal. Chem. 6, 129; it was criticised and rejected in MOHR's Lehrb. d. Titrirmethode 3 Aufl. 291. OUDEMANS replied to MOHR in Zeitschr. f. anal. Chem. 9, 342, and an examination of the method by C. BALLING, appeared in the same journal, 9, 99.

In the analysis the conditions should be similar to those in the standardizing of the hyposulphite.

This method is very rapid, and the results, though not so accurate as those by methods *a* and *β*, are quite good enough for many technical purposes.

Supplement to §§ 112 *and* 113.

Besides the methods given in §§ 112 and 113, there are several others, especially indirect methods, by which the estimation of iron may be effected; some of these are old, others have been proposed lately. However, as they either are in no way superior to those already described, or find only limited application, I confine myself here to a mere brief description of the most important among them.

1. FUCHS'S method.* The solution, which contains the iron as *sesquioxide*, and must be free from nitric acid, is mixed with hydrochloric acid, and boiled with weighed strips of metallic copper, until the fluid has become light green; the quantity of iron is estimated from the loss of weight of the copper ($Fe_2Cl_3 + 2Cu = 2FeCl + Cu_2Cl$). The method only yields satisfactory results on the most careful exclusion of the air. The circumstances most favourable to success have been studied by LÖWE and KÖNIG, and will be described in detail, under the "Analysis of Iron Ores," in the Special Part.

2. The solution, which contains the iron as *sesquioxide*, and must be free from metals of the fifth and sixth groups, as well as from other substances exercising a decomposing action upon sulphuretted hydrogen, is precipitated with clear sulphuretted hydrogen water in excess, all application of heat being avoided. After a few days the precipitated sulphur is determined, and the amount of sesquioxide of iron calculated therefrom ($Fe_2O_3 + HS = 2FeO + HO + S$) (H. ROSE). Results accurate, compare DELFFS.†

3. The solution, which contains the iron as *protoxide*, is mixed with sodio-terchloride of gold in excess, the flask closed, and the reduced gold which separates determined. $6FeCl + AuCl_3 = 3Fe_2Cl_3 + Au$ (H. ROSE).

§ 114.

Supplement to the Fourth Group.

7. SESQUIOXIDE OF URANIUM.

If the compound in which the uranium is to be determined contains no other fixed substances, it may often be converted into *protosesquioxide* (UO,U_2O_3) by simple ignition. If sulphuric acid is present, small portions of carbonate of ammonia must be thrown into the crucible towards the end of the operation.

In cases where the application of this method is inadmissible, the solution of uranium (which, if it contains protoxide, must first be warmed with nitric acid, until the protoxide is converted into sesquioxide) is nearly boiled in a platinum or porcelain dish, and precipitated with ammonia in slight excess. The yellow precipitate formed, which consists of hydrated *ammonio-sesquioxide of uranium*, is filtered off hot and washed with a dilute solution of chloride of ammonium, to prevent the fluid passing milky through the filter. The precipitate is dried and ignited (§ 53). To make quite sure of obtaining the protosesquioxide in the pure state, the crucible is ignited for some time in a slanting position and uncovered; the lid is then put on, while the ignition is still continuing; the crucible is allowed to cool under the desiccator, and weighed (RAMMELSBERG).

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* Journ. f. prakt. Chem. 17, 160.

† Chem. Centralbl. 1856, 839.

If the solution from which the sesquioxide of uranium is to be precipitated contains other bases (alkaline earths, or even alkalies), portions of these will precipitate along with the ammonio-sesquioxide of uranium. For the measures to be resorted to in such cases, I refer to Section V.

The reduction of the protosesquioxide of uranium to the state of protoxide (UO) is an excellent means of ascertaining its purity for the purpose of control. This reduction should never be omitted, since PÉLIGOT has found the protosesquioxide to be variable in composition. It is effected by ignition in a current of hydrogen gas, in the way described § 111, 1 (Cobalt). In the case of large quantities the ignition must be several times repeated, and the residue must be occasionally stirred with a platinum wire. While cooling increase the current of gas to prevent reabsorption of oxygen. By intense heating the property of spontaneous ignition in the air is destroyed. If after evaporating a solution of sesquichloride of uranium, the residue is to be ignited in hydrogen; heat gently at first in the gas to avoid the loss of small quantities of oxychloride. The separation of sesquioxide of uranium from phosphoric acid is effected by fusing the compound with cyanide of potassium and carbonate of soda. Upon extracting the fused mass with water, the phosphoric acid is obtained in solution, whilst the uranium is left as protoxide. KNOP and ARENDT* have employed this method.

The equivalent of protosesquioxide of uranium = 210·2, viz., 178·2 of uranium and 32 of oxygen. In 100 parts, the compound consists of 84·77 of uranium and 15·23 of oxygen. The equivalent of protoxide of uranium is 67·4, viz., 59·4 of uranium and 8 of oxygen; in 100 parts, the protoxide consists of 88·13 of uranium and 11·87 of oxygen.

According to BELOHOUBECK,† uranium may be also determined volumetrically by reducing the solution of the sesquisulphate or acetate with zinc, as in the case of iron (§ 113, 3, *a*). As the color of the solution is no safe criterion of the end of the reduction, you must allow the action of the zinc to continue for a considerable time. BELOHOUBECK says, a quarter of an hour is sufficient for small quantities, half an hour for large quantities. The solution of the protoxide is diluted, mixed with dilute sulphuric acid, and then titrated with permanganate to incipient reddening. The permanganate is standardized by § 112, 2, 1 eq. uranium = 1 eq. iron.

BELOHOUBECK obtained good results also in hydrochloric solutions, but experiments made in this laboratory have shown that these are liable to the error pointed out in the case of iron (Comp. p. 219, γ), at least in the presence of considerable quantities of hydrochloric acid.

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* Chem. Centralblatt, 1856, 773.

† Zeitschr. f. anal. Chem. 6, 120.

FIFTH GROUP.

OXIDE OF SILVER—OXIDE OF LEAD—SUBOXIDE OF MERCURY—OXIDE OF MERCURY—OXIDE OF COPPER—TEROXIDE OF BISMUTH—OXIDE OF CADMIUM—(PROTOXIDE OF PALLADIUM).

§ 115.

1. Oxide of Silver.

a. Solution.

Metallic silver, and those of its compounds which are insoluble in water, are best dissolved in nitric acid (if soluble in that acid). Dilute nitric acid suffices for most compounds; sulphide of silver, however, requires concentrated acid. The solution is effected best in a flask, which should be heated if necessary, and placed in a slanting position if gas is evolved. In the case of metallic silver, or sulphide of silver, the solution is heated finally to gentle boiling to drive off nitrous acid. Chloride, bromide, and iodide of silver are insoluble in water and in nitric acid. To get the silver contained in chloride and bromide in solution, proceed as follows:—Fuse the salt in a porcelain crucible (this operation, though not absolutely indispensable, had better not be omitted), pour water over it, put a piece of clean cadmium, zinc, or iron upon it, and add some dilute sulphuric acid. Wash the reduced spongy silver, first with dilute sulphuric acid, then with water, and finally dissolve it in nitric acid. However, as we shall see below, the quantitative analysis of these salts does not necessarily involve their solution.

b. Determination.

Silver may be weighed as *chloride*, *sulphide*, or *cyanide*, or in the *metallic* state (§ 82). It is also frequently determined by volumetric analysis.

We may convert into

1. Chloride of silver: All compounds of silver without exception.

2. Sulphide of silver: 3. Cyanide of silver: All compounds soluble in water or nitric acid.

4. Metallic silver: Oxide of silver, and some of its compounds with readily volatile acids; salts of silver with organic acids; chloride, bromide, iodide, sulphide, and sulphate of silver.

The method 4 is the most convenient, especially when conducted in the dry way, and is preferred to the others in all cases where its application is admissible. The method 1 is that most generally resorted to. 2 and 3 serve mostly only to effect the separation of oxide of silver from other bases.

In assays for the Mint, silver is usually determined volumetrically by Gay-Lussac's method. Pisani's volumetric method is especially suited to the determination of very small quantities of silver. H. Vogel's method is specially useful to photographers. The estimation of silver by cupellation will be described in the Special Part, under the Analysis of Galena.

1. *Determination of Silver as Chloride.*

a. In the Wet Way.

Mix the moderately dilute solution in a beaker with nitric acid, heat to about 70°, and add hydrochloric acid with constant stirring till it ceases to produce a precipitate. A large excess of hydrochloric acid must be avoided, as the precipitate is not absolutely insoluble therein. While protecting the contents of the beaker from the action of direct sunlight continue the heat till the precipitate has fully settled, pour off the clear fluid through a small filter, rinse the precipitate on to the latter by means of hot water mixed with some nitric acid, wash with hot water containing nitric acid, then with pure hot water, dry thoroughly, transfer the precipitate to a watch-glass as nearly as possible, incinerate the filter in a weighed porcelain crucible, treat the ash (which always contains some metallic silver) with a few drops of nitric acid in the heat; add two or three drops of hydrochloric acid, evaporate cautiously to dryness, add the main bulk of the precipitate, using a camel's hair brush to transfer the last portions, heat cautiously till it begins to fuse at the edge, allow to cool, and weigh.

To remove the fused mass without breaking the crucible, lay a small piece of iron or zinc upon it, and then add very dilute hydrochloric or sulphuric acid. The chloride will be reduced, and the silver may now be detached from the crucible with the greatest ease.

For the properties of the precipitate see § 82. The method gives very exact results, at all events in the absence of any considerable quantities of those salts in which chloride of silver is somewhat soluble; compare § 82. To avoid error in this respect, it is well to test the clear filtrate with sulphuretted hydrogen.

b. In the Dry Way.

This method serves more exclusively for the analysis of bromide and iodide of silver, although it can be applied in the case of other compounds. The process is conducted in the apparatus illustrated by fig. 83.

a is an apparatus for disengaging chlorine; *b* contains concentrated sulphuric acid, *c* chloride of calcium; *d* is a bulb-tube intended for the reception of the iodide or bromide of silver; and *e* serves to conduct the chlorine gas into the open air, or into a flask containing hydrate of lime. The operation is commenced by introducing the compound to be analysed into the bulb, and applying heat to the latter until its contents are fused; when cold, the tube is weighed and connected with the apparatus. Chlorine gas is then evolved from *a*; when the evolution of the gas has proceeded for some time, the contents of the bulb are heated to fusion, and kept in this state for about fifteen minutes, agitating now and then the fused mass. The bulb-tube is then removed from the apparatus, allowed to cool, and held in a slanting position to replace the chlorine by atmospheric air; it is subsequently weighed, then again connected with the apparatus, and the former process repeated, keeping the contents of *d* in a state of fusion for a few minutes. The operation may, in ordinary cases, be considered concluded if the weight of the tube suffers no variation by the repetition of the process. If the highest degree of accuracy is to be attained, heat the chloride of silver again to fusion, passing at the same time a slow stream of pure, dry, carbonic acid through the tube, in order to drive out the traces of chlorine absorbed by the fused chloride. Allow to cool, hold obliquely for a short time, so as to replace the carbonic acid by air, and finally weigh.

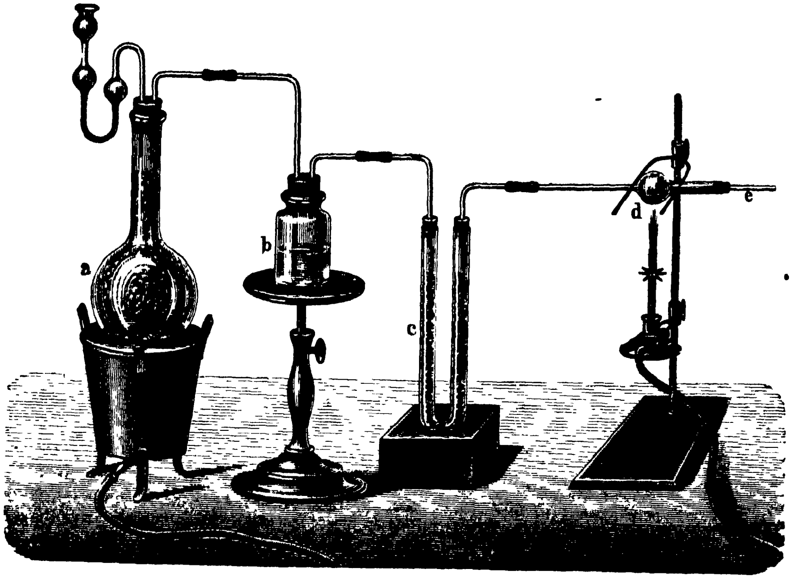

Fig. 83.

2. *Determination as Sulphide of Silver.*

Sulphuretted hydrogen precipitates silver completely from acid, neutral, and alkaline solutions; sulphide of ammonium precipitates it from neutral and alkaline solutions. The precipitate does not settle clearly and rapidly except a free acid or salt be present (such as nitric acid or an alkaline nitrate). Recently prepared perfectly clear solution of sulphuretted hydrogen may be employed to precipitate small quantities of silver; to precipitate larger quantities, the solution of the salt of silver (which must not be too acid) is moderately diluted, and washed sulphuretted hydrogen gas conducted into it. After complete precipitation has been effected, and the sulphide of silver has perfectly subsided (with exclusion of air) it is collected on a weighed filter, washed, dried at 100°, and weighed. For the properties of the precipitate, see § 82. This method, if properly executed, gives accurate results. The operator must take care to filter quickly, and to prevent the access of air as much as possible during the filtration, since, if this precaution be neglected, sulphur is likely to separate from the sulphuretted hydrogen water, which, of course, would add falsely to the weight of the sulphide of silver. If the presence of a minute quantity of sulphur in the precipitate is suspected, treat it after drying with pure bisulphide of carbon on the filter repeatedly, till the fluid running through gives no residue on evaporation in a watch-glass; dry and weigh.

The sulphide must, however, never be weighed as just described, unless the analyst is satisfied that no considerable amount of sulphur has fallen down with it, as would occur if the fluid contained hyponitric acid, sesquioxide of iron, or any other substance which decomposes sulphuretted hydrogen. In case the precipitate does contain much admixed sulphur, the simplest process is to convert it into metallic silver (H. ROSE*). For this purpose it is transferred to a weighed porcelain crucible, the filter ash is added, and the whole is heated to redness in a stream of hydrogen, the apparatus described in § 108 being employed. Results accurate.

Should the apparatus in question not be at the operator's disposal, he may, after complete washing of the precipitate, carefully rinse it into a porcelain dish (without injuring the weighed filter), heat it once or twice with a moderately strong solution of pure sulphite of soda, retransfer the precipitate (now freed from admixed sulphur) to the old filter, wash well, dry and weigh (J. LÖWE†); or he may treat the dried precipitate, together with the filter-ash, with moderately dilute chlorine-free nitric acid at a gentle heat, till complete decomposition has been effected (till the undissolved sulphur has a clean yellow appearance), filter, wash well, and proceed according to 1, *a*.

3. *Determination as Cyanide of Silver.*

Mix the neutral solution of silver with cyanide of potassium, until the precipitate of cyanide of silver which forms at first is redissolved; add nitric acid in slight excess, and apply a gentle heat. If the solution contains free acid, this must be first neutralized with potash or carbonate of soda. After some time, collect the precipitated cyanide of silver on a weighed filter, wash, dry at 100°, and weigh. For the properties of the precipitate, see § 82. The results are accurate.

4. *Determination as Metallic Silver.*

a. In the Dry Way.

Oxide of silver, carbonate of silver, &c., are easily reduced by simple ignition in a porcelain crucible. In the reduction of salts with organic acids, the crucible is kept covered at first, and a moderate heat applied; after a time the lid is removed, and the heat increased, until the whole of the carbon is consumed. For the properties of the residue, see § 82. The results are absolutely accurate, except as regards salts of silver with organic acids; in the analysis of the latter, it not unfrequently happens that the reduced silver contains a minute portion of carbon, which increases the weight of the residue to a trifling extent.

If it is desired to transform chloride, bromide, or sulphide of silver into metallic silver, for the purpose of analysis, they are heated in a current of pure hydrogen to redness, till the weight remains constant. The process may be conducted in a porcelain crucible or a bulb-tube. In the former case, the apparatus described § 108, fig. 79, is used; in the latter the apparatus represented p. 233, with the substitution, of course, of hydrogen for chlorine. If the bulb-tube is used, it must, after cooling and before being weighed, be held in an inclined position, so that the hydrogen may be replaced by air. The results are perfectly accurate. Iodide of silver cannot be reduced in this way.

b. In the Wet Way.

If the solution contains nitric acid add sulphuric acid, evaporate till all the nitric acid is driven off, dissolve the sulphate of silver in hot water, transfer to a weighed porcelain crucible, and place therein a rod of cadmium. The reduction soon takes place, and the separated metal may be readily removed from the cadmium and united to a coherent mass. Warm the latter with the acid fluid till hydrogen ceases to escape, wash with hot water by decantation, dry and ignite. Results accurate (A. CLASSEN*). Cadmium is preferable to zinc, as the latter generally leaves behind a little lead when dissolved in dilute sulphuric acid.

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* Pogg. Annal. 110, 139.

† Journ. f. prakt. Chem. 77, 73.

5. *Volumetric Methods.*

I. GAY-LUSSAC'S.

This, the most exact of all known volumetric processes, was introduced by GAY-LUSSAC as a substitute for the assay of silver by cupellation, was thoroughly investigated by him, and will be found fully described in his work on the subject. This method has been rendered still more precise by the researches of G. J. MULDER, to whose exhaustive monograph† I refer the special student of this branch. I shall here confine myself to giving the process so far as to suit the requirements of the chemical laboratory, taking only for granted that the analyst has the ordinary measuring apparatus, &c., at his disposal. MULDER'S results will be made use of to the full extent possible under these circumstances.

a. REQUISITES.

α. SOLUTION OF CHLORIDE OF SODIUM. Take chemically pure chloride of sodium—either artificially prepared or pure rock-salt—powder it roughly and ignite moderately (not to fusion‡). Now dissolve 5·4202 grm. in distilled water to 1 litre, measured at 16°. 100 c.c. of this solution contains a quantity of chloride of sodium equivalent to 1 grm. of silver. The solution is kept in a stoppered bottle and shaken before use.

β. DECIMAL SOLUTION OF CHLORIDE OF SODIUM. Transfer 50 c.c. of the solution described in *α* to a 500 c.c. measuring flask, fill up to the mark with distilled water and shake. Each c.c. of this decimal solution corresponds to ·001 grm. silver. The measuring must be performed at 16°. The solution is kept as the other.

γ. DECIMAL SILVER SOLUTION. Dissolve ·5 grm. chemically pure silver§ in 2 to 3 c.c. pure nitric acid of 1·2 sp. gr., and dilute the solution with water exactly to 500 c.c. measured at 16°. Each c.c. contains ·001 grm. silver. The solution is kept in a stoppered bottle and protected against the influence of light.

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* Zeitschr. f. anal. Chem. 5, 402. The method proposed by MILLON and COMMAILLE (*Ib.* 2, 212) of precipitating the silver with ammonio-subchloride of copper has been tested by STAS (*Ib.* 6, 426) and also by myself, and not found worthy of recommendation.

† Die Silberprobirmethode (see note p. 139).

‡ On fusion, if the flame can in the least way act upon it, it takes an alkaline reaction, since under the influence of vapor of water and carbonic acid, a little hydrochloric acid is formed and escapes, while a corresponding quantity of carbonate of soda remains.

§ For the preparation of pure silver STAS recommends the following method: Take crude nitrate of silver containing copper, fuse in order to decompose any nitrate of platinum which may be present, dissolve in dilute ammonia, allow to stand 48 hours, filter and dilute till the fluid does not contain more than 2 per cent. silver. Add sulphite of ammonia in excess. To ascertain how much sulphite will be required make a small preliminary test; as soon as after heating the blue solution loses all color, you may be sure that enough of the sulphite has been added. Warm on a water-bath to 60° or 70°, when all the silver will be thrown down as a metallic powder, allow to cool and wash by decantation with diluted ammonia till the washings are free from copper and sulphuric acid. Now digest the metal for several days with strong ammonia, wash, dry, and fuse with a flux of borax and nitrate of soda.

δ. TEST-BOTTLES. These should be of colorless glass, holding easily 200 c.c., closed with well-ground glass-stoppers, running to a point below. The bottles fit into cases blackened on the inside, and reaching up to their necks. In order to protect the latter also from the action of light, a black-cloth cover is employed.

b. PRINCIPLE.

Suppose we know the value of a solution of chloride of sodium, *i.e.*, the quantity that is necessary to precipitate a given amount of silver, say 1 grm., we are in the position, with the aid of this solution, to determine an unknown amount of silver, for if we put x for the unknown amount of silver, then

$$\text{c.c. of solution used for 1 grm.} : \text{c.c. used for } x :: 1 \text{ grm.} : x.$$

But if we examine whether 1 eq. chloride of sodium dissolved in water actually precipitates 1 eq. of silver dissolved in nitric acid exactly, we find that this is not the case.* On the contrary, the clear supernatant fluid gives a small precipitate both on the addition of a little solution of chloride of sodium, and on the addition of a little silver solution, as MULDER has most accurately determined. The value of a solution of chloride of sodium in the sense explained above cannot, therefore, be reckoned from the amount of salt it contains, by calculating 1 eq. silver for 1 eq. chloride of sodium, but it can only be obtained by experiment. MULDER has shown that the temperature and the degree of dilution have some influence, and also that this fact is to be explained on the ground of the solvent power of the nitrate of soda produced on the chloride of silver. In the solution thus formed we have to imagine NaO,NO_5 and $NaCl$ with AgO,NO_5 in a certain state of equilibrium, which on the addition of either $NaCl$ or AgO,NO_5 is destroyed, chloride of silver being precipitated.

From this interesting observation it follows, that if to a silver-solution we add at first concentrated solution of chloride of sodium, then decimal solution drop by drop, till the exact point is reached when no more precipitate appears, now, on addition of decimal silver-solution, a small precipitate will be again produced; and if we add the latter drop by drop, till the last drop occasions no turbidity, then again decimal solution of chloride of sodium will give a small precipitate. On noticing the number of drops of both decimal solutions which are required to pass from one limit to the other, we find that the same number of each are used. Let us suppose that we had added decimal solution of chloride of sodium till it ceased to react, and had then used 20 drops† of decimal silver-solution, till this ceased to produce a further turbidity, we must now again add 20 drops of decimal solution of chloride of sodium, in order to reach the point at which this ceases to react. Were we to add only 10 instead of these 20 drops, we have the neutral point, as MULDER calls it, *i.e.*, the point at which both silver and chloride of sodium produce equal precipitates.

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* If bromide of sodium or potassium is used, complete precipitation would ensue on addition of an equivalent quantity of silver solution, since bromide of silver is not at all soluble in the supernatant fluid (STAS, Compt. rend. 67, 1107).

† Twenty drops from MULDER'S dropping apparatus are equal to 1 c.c.

We have, therefore, 3 different points to choose from for our final reaction: *a*, the point at which chloride of sodium has just ceased to precipitate the silver; *b*, the neutral point; *c*, the point at which silver-solution has just ceased to precipitate chloride of sodium. Whichever we may choose, we must keep to it, *i.e.*, we must not use a different point in standardizing the chloride of sodium solution and in performing an analysis. The difference obtained, by using first *a* and then *b* is, according to MULDER, for 1 grm. silver, at 16°, about ·5 mgrm. silver; by employing first *a* and then *c*, as was permitted in the original process of GAY-LUSSAC, the difference is increased to 1 mgrm.

For our object, it appears most convenient to consider, once for all, the point *a* as the end, and never to finish with the silver-solution. If the point has been overstepped by the addition of too large an amount of decimal solution of chloride of sodium, 2 or 3 c.c. of decimal silver-solution should be added all at once. The end-point is then found by carefully adding decimal solution of chloride of sodium again, and the quantity of silver in the silver-solution added is added to the original amount of silver weighed off.

c. PERFORMANCE OF THE PROCESS.

This is divided into two operations—*α*, the titration of the chloride of sodium solution; *β*, the assay of the silver alloy to be examined.

α. TITRATION OF THE CHLORIDE OF SODIUM SOLUTION.

Weigh off exactly from 1·001 to 1·003 grm. chemically pure silver,* put it into a test-bottle, add 5 c.c. perfectly pure nitric acid, of 1·2 sp. gr., and heat the bottle in an inclined position in a water- or sand-bath till complete solution is effected. Now blow out the nitrous fumes from the upper part of the bottle, and after it has cooled a little, place it in a stream of water, the temperature of which is about 16°, and let it remain there till its contents are cooled to this degree, wipe it dry, and place it in its case.

Now fill the 100 c.c. pipette with the concentrated solution of chloride of sodium, which is then allowed to flow into the test-bottle containing the silver-solution.† Insert the glass-stopper firmly (after moistening it with water), cover the neck of the bottle with the cap of black stuff belonging to it, and shake violently without delay, till the chloride of silver settles, leaving the fluid perfectly clear. Then take the stopper out, rub it on the neck, so as to remove all chloride of silver, replace it firmly, and by giving the bottle a few dexterous turns, rinse the chloride down from the upper part. After allowing to rest a little, again remove the stopper, and add, from a burette divided into $\frac{1}{10}$ c.c., decimal chloride of sodium solution, allowing the drops to fall against the lower part of the neck, the bottle being held in an inclined position. If, as above directed, 1·001 to 1·003 grm. silver have been employed, the portions of chloride of sodium solution at first added may be ½ c.c. After each addition, raise the bottle a little out of its case, observe the amount of precipitate produced, shake till the fluid has become clear again, and proceed as above, before adding each fresh quantity of chloride of sodium solution. The smaller the precipitate produced, the smaller should be the quantity of chloride of sodium next added; towards the end only two drops should be added each time; and quite at the end read off the height of the fluid in the burette before each further addition. When the last two drops give no more precipitate, the previous reading is the correct one.

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* See note, p. 235.

† The pipette, having been filled above the mark, should be fixed in a support, before the excess is allowed to run out, otherwise the measurings will not be sufficiently accurate.

If by chance the point has been overstepped, and the time has been missed for the proper reading off of the burette, add 2 to 3 c.c. of the decimal silver solution (the silver in which is to be added to the quantity first weighed), and try again to hit the point exactly by careful addition of decimal chloride of sodium solution.

The value of the chloride of sodium solution is now known. Reckon it to 1 grm. silver.

Suppose we had used for 1·002 grm. silver, 100 c.c. of concentrated and 3 c.c. of decimal chloride of sodium solution; this makes altogether 100·3 of concentrated; then

$$1{\cdot}002 : 1{\cdot}000 :: 100{\cdot}3 : x$$
$$x = 100{\cdot}0998$$

We may without scruple put 100·1 for this number. We now know that 100·1 c.c. of the concentrated solution of chloride of sodium, measured at 16°, exactly precipitates 1 grm. of silver. This relationship serves as the foundation of the calculation in actual assaying, and must be re-examined whenever there is reason to imagine that the strength of the chloride of sodium solution may have altered.

β. THE ACTUAL ASSAY OF THE SILVER-ALLOY.

Weigh off so much as contains about 1 grm. of silver, or better, a few mgrm. more;* dissolve in a test-bottle in 5 to 7 c.c. nitric acid, and proceed in all respects exactly as in *a*.

Suppose we had taken 1·116 grm. of the alloy, and in addition to the 100 c.c. of concentrated chloride of sodium solution, had used 5 c.c. of the dilute (= ·5 concentrated), how much silver would the alloy contain?

Presuming that we use the same chloride of sodium solution which served as our example in *a*, 100·1 c.c. of which = 1 grm. silver, then

$$100{\cdot}1 : 100{\cdot}5 :: 1{\cdot}000 : x$$
$$x = 1{\cdot}003996 \text{ (say } 1{\cdot}004).$$

We may also arrive at the same result in the following manner:—

	NaCl Solution.
For the precipitation of the silver in the alloy were used	100·5 c.c.
For 1 grm. silver are necessary	100·1 c.c.
Difference	·4 c.c.

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* In coins containing 9 parts of silver and 1 part of copper, therefore take about 1·115 or 1·120. In weighing off alloys of silver and copper, which do not correspond to the formula Ag_3Cu_4 (standard = $\frac{718{\cdot}67}{1000}$), we must remember that they are never homogeneous in the mass; thus, for instance, the pieces of metal, from which coins are stamped, often show 1·5 to 1·7 in a thousand more silver in the middle than at the edges. In assaying alloys, then, portions from various parts of the mass must be taken, in order to get a correct result. The inaccuracy, however, proceeding from the cause above-mentioned, can only be completely overcome by fusing the alloy and taking out a portion from the well-stirred mass for the assay.

There are, therefore, 4 mgrm. of silver present more than a grm., on the presumption that ·1 of the concentrated chloride of sodium solution (= 1 c.c. of the decimal solution) corresponds to 1 mgrm. silver. This supposition, although not absolutely correct, may be safely made, for the inexactness it involves is too minute, as is evident from the previous calculation.

Before we can execute this process exactly, we must know the quantity of silver the alloy contains very approximately. In assaying coins of known value this is the case, but with other silver alloys it is usually not so. Under the latter circumstances an approximate estimation must precede the regular assay. This is performed by weighing off $\frac{1}{2}$ grm. (or in the case of alloys that are poor in silver, 1 grm.), dissolving in 3 to 6 c.c. nitric acid, and adding from the burette chloride of sodium solution,—first in larger, then in smaller quantities—till the last drops produce no further turbidity. The last drops are not reckoned with the rest. The operation is conducted, as regards shaking, &c., as previously given. Suppose we had weighed off ·5 grm. of the alloy, and employed 25 c.c. of the chloride of sodium solution—taking the above supposed value of the latter—

We have $100·1 : 25 : : 1·000 : x$

$x = ·2497$

that is, the silver in ·5 grm. of the alloy; and as to the quantity of alloy we have to weigh off for the assay proper,

We have $·2497 : 1·003 : : ·5 : x$

$x = 2·008.$

This quantity will, of course, require more nitric acid for solution than was previously used (use 10 c.c.). In cases where the highest degree of accuracy is not required, the results afforded by this rough preliminary estimation will be accurate enough, if the experiment is carefully conducted, since they give the quantity of silver present to within $\frac{1}{1000}$ or $\frac{1}{500}$.

With alloys which contain sulphur, and with such as consist of gold and silver, and contain a little tin, Levol* employs concentrated sulphuric acid (about 25 grm.) as solvent. The portion of the alloy is boiled with it till dissolved; after cooling, the fluid is treated in the usual manner. As, however, concentrated sulphuric acid fails to dissolve all the silver when there is much copper present, Mascazzini† digests the weighed portion of alloy (which may contain small quantities of lead, tin, and antimony, besides gold) first with the least possible amount of nitric acid, as long as red vapors are formed; he then adds concentrated sulphuric acid, boils till the gold has settled well together, adds water after cooling, and then titrates. In the presence of mercury, the chloride of that metal is carried down with the silver, rendering the method inaccurate. If the quantity of mercury is but small, you may get over the difficulty by adding 25 c.c. ammonia and 20 c.c. acetic acid (Levol). The acetate of ammonia acts by decomposing the chloride of mercury, and thus preventing its precipitation (Debray‡). If the quantity of mercury is large the addition of an alkaline acetate is not effective, and Debray recommends to drive off the mercury by igniting for four hours in a small crucible of gas carbon in a muffle. The presence of other volatile metals, such as zinc, does not interfere with this operation.

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* Annal. de Chim. et de Phys. (3) 44, 347.

† Chem. Centralbl. 1857, 300.

‡ Compt. rend. 70, 849.

II. PISANI'S METHOD.*

This process depends on the following reaction: a solution of iodide of starch added to a very dilute neutral solution of nitrate of silver, forms iodide of silver and hypoiodite of silver. The blue color consequently vanishes, and on continued addition of the iodide of starch, the fluid does not become permanently blue till all the nitrate of silver present is decomposed in the above manner. The iodide of starch solution used is therefore proportional to the quantity of nitrate of silver. Hence, if the value of the iodide of starch solution be determined, by allowing it to act on a certain amount of silver solution of known strength, we shall be able to estimate unknown quantities of silver with the greatest ease, provided that the silver solution is free from all other substances which exert a decomposing action on the iodide of starch. Besides the ordinary reducing agents, the following salts must be especially mentioned as possessing this power: the salts of suboxide and protoxide of mercury, of protoxide of tin, of teroxide of antimony, of arsenious acid, of protoxide of iron and of protoxide of manganese, also chloride of gold; salts of lead and of copper, on the other hand, do not affect iodide of starch.

The iodide of starch is prepared as follows: make an intimate mixture in a mortar of 2 grm. iodine and 15 grm. starch with the addition of 6 to 8 drops of water, and heat the slightly-moist mixture in a closed flask in a water-bath, till the original violet-blue color has passed into dark grayish-blue—it takes about an hour. The iodide of starch thus prepared is then digested with water; it dissolves completely to a deep bluish-black fluid.

The value of this fluid is determined by allowing it to act on 10 c.c. of a neutral solution of nitrate of silver, containing 1 grm. of pure silver in 1 litre,—the silver solution is mixed with a little pure precipitated carbonate of lime before adding the iodide of starch. The strength of this latter is right, if 50 to 60 c.c. are used in this experiment. On adding it, at first the blue color disappears rapidly, and the fluid becomes yellowish from the iodide of silver. The end of the operation is attained as soon as the fluid is bluish-green. The point is pretty easy to hit, and an error of ·5 c.c. is of no importance, as it only corresponds to about ·0001 grm. silver. The carbonate of lime, besides neutralizing the free acid, has the effect of rendering the final change of the color more distinctly observable. To analyse an alloy of silver and copper, dissolve about ·5 grm. in nitric acid, dilute to 100 c.c. to lower the color of the copper, saturate 5 c.c. with carbonate of lime, and add iodide of starch till the coloration appears. Or, you may determine very approximately the amount of silver in 2 c.c. of the solution, then precipitate the greater part (about 99%) of the silver from 50 c.c. of the solution with standard solution of iodide of potassium and without filtering estimate the remainder of the silver by means of iodide of starch. If the amount of silver to be determined is more than ·020 grm., it is always better to employ the latter method. In the case of a nitric acid solution containing silver with lead, the latter metal is first precipitated with sulphuric acid and filtered off, carbonate of lime is added to the filtrate till all free acid is neutralized, the fluid is filtered again (if necessary), and lastly, more carbonate of lime is added, and then the iodide of starch. Very dilute solutions must be concentrated, so that one may have no more than from 50 to 100 c.c. to deal with. The method is worthy of notice and specially suited for the estimation of small quantities of silver. With such it has afforded me perfectly satisfactory results. Instead of the standard iodide of starch, a dilute standard solution of iodine in iodide of potassium may be equally well employed,—with addition of starch solution (FIELD[*]). If this is used you must bear in mind that any substance which decomposes iodide of potassium with separation of iodine will interfere.

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* Annal. d. Min. 10, 83.

The above method has been modified by H. VOGEL[†] mainly with the view of adapting it to the use of photographers. To the silver solution, which may contain free acid, nitric acid containing nitrous acid is added; the latter being prepared by mixing 1000 grm. nitric acid of 1·2 sp. gr. with 1 grm. sulphate of iron. Starch solution is also added, and then standard solution of iodide of potassium till a permanent blue color is produced. This of course does not occur till the whole of the silver is precipitated, partly as iodide, partly as iodate. The decomposition is as follows: $KI + AgO,NO_5 = KO,NO_5 + AgI$ and $I_6 + 6AgO,NO_5 = AgO,IO_5 + 5AgI$. In both cases 1 eq. iodine precipitates 1 eq. silver. The standard solution is prepared by dissolving 10 grm. pure dry iodide of potassium to 1023·4 c.c.; 1 c.c. indicates ·01 grm. silver. From my own experiments it appears that the method is expeditious but not accurate. The same quantities of silver will require distinctly varying quantities of iodide of potassium when the conditions are altered, especially the concentration and the amount of free nitric acid; this is evidently connected with the formation of iodate of silver which is not quite insoluble in the acid fluid.

III. METHOD DEPENDING ON THE ACTION OF NITRATE OF SILVER ON CHLORIDE OF SODIUM IN THE PRESENCE OF CHROMATE OF POTASSIUM.

This is the reverse of the method for the estimation of chlorine § 141, *b*, *a*, and will be described in that place.

§ 116.

2. OXIDE OF LEAD.

a. Solution.

Few of the salts of lead are soluble in water. Metallic lead, oxide of lead, and most of the salts of lead that are insoluble in water dissolve in *dilute* nitric acid. Concentrated nitric acid effects neither complete decomposition nor complete solution, since, owing to the insolubility of nitrate of lead in concentrated nitric acid, the first portions of nitrate formed protect the yet undecomposed parts of the salt from the action of the acid. For the solubility of chloride and sulphate of lead, see § 83. As we shall see below, the analysis of these compounds may be effected without dissolving them. Iodide of lead dissolves readily in moderately dilute nitric acid upon application of heat, with separation of iodine. Solution of potassa is the only menstruum in which chromate of lead dissolves without decomposition; for the purpose of analysis, the chromate is best converted into the chloride (see below).

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[*] Chem. News, 2, 17.

[†] Pogg. Ann. 124, 347; Zeitschr. f. anal. Chem. 5, 227.

b. Determination.

Lead may be determined as *oxide*, *sulphate*, *chromate*, *sulphide*, *chloride*, as *oxide of lead + lead*, or as *lead*; also by volumetric analysis.

We may convert into

1. OXIDE OF LEAD:

a. By Precipitation. All salts of lead soluble in water, and those of its salts which, insoluble in that menstruum, dissolve in nitric acid, with separation of their acid.

b. By Ignition.

α. Salts of lead with readily volatile or decomposable inorganic acids.

β. Salts of lead with organic acids.

2. SULPHIDE OF LEAD: All salts of lead in solution.

3. SULPHATE OF LEAD:

a. By Precipitation. The salts that are insoluble in water, but soluble in nitric acid, whose acid cannot be separated from the solution.

b. By Evaporation.

α. All the oxides of lead, and also the salts of lead with volatile acids.

β. Many of the organic compounds of lead.

4. CHROMATE OF LEAD: The compounds of lead soluble in water or nitric acid.

5. CHLORIDE OF LEAD: Chromate of lead.

6. OXIDE OF LEAD + LEAD: Many of the organic compounds of lead.

7. LEAD: The oxides and most of the salts of lead including the chloride, bromide and iodide.

The volumetric methods are rarely available.

The application of these several methods must not be understood to be rigorously confined to the compounds specially enumerated under their respective heads; thus, for instance, all the compounds enumerated under 1, may likewise be determined as sulphate of lead; and, as above mentioned, all soluble compounds of lead may be converted into sulphide of lead. Chloride, bromide, and iodide of lead may be decomposed by boiling with solution of carbonate of soda; by passing carbonic acid through the solution after cooling, the small quantity of lead retained will be precipitated. The higher oxides of lead are reduced by ignition to the state of simple oxide, and may thus be readily analysed and dissolved. Should the operator wish to avoid having recourse to ignition, the most simple mode of dissolving the higher oxides of lead is to act upon them with dilute nitric acid, with the addition of alcohol. For the methods of analysing sulphate and chromate of lead, I refer to the paragraphs treating of the corresponding acids, in the second part of this Section.

1. *Determination as Oxide.*

a. By Precipitation.

Mix the moderately dilute solution with carbonate of ammonia slightly in excess, add some caustic ammonia, apply a gentle heat, allow to cool and filter through a small thin filter. Wash with pure water, dry, and transfer the precipitate to a watch-glass, removing it as completely as possible from the filter; burn the latter in a weighed porcelain crucible. After the crucible is cold, moisten the ash with nitric acid, allow it to evaporate, ignite gently, allow to cool, add the precipitate and ignite gently till all the carbonic acid is driven off. For the properties of the precipitate and residue, see § 83. The results are very satisfactory, although generally a trifle too low, owing to carbonate of lead not being absolutely insoluble, particularly in fluids rich in ammoniacal salts (Expt. No. 42, *b*).

b. By Ignition.

Compounds like carbonate or nitrate of lead are cautiously ignited in a porcelain crucible, until the weight remains constant. Nitrate of lead must be very completely dried, before being ignited, or loss may occur from decrepitation. For the manner of converting salts of lead with organic acids into oxide, see 6.

2. *Determination as Sulphide.*

Lead may be completely precipitated from acid, neutral and alkaline solutions by sulphuretted hydrogen, and also from neutral and alkaline solutions by sulphide of ammonium. Precipitation from acid solution is usually employed, especially in separations. A large excess of acid and also warming should both be avoided. The former is prejudicial to complete precipitation (§ 83, *f*), the latter may readily occasion the resolution of the sulphide that has already been precipitated. In order to guard against incomplete precipitation, before filtering, test a portion of the supernatant fluid by mixing with a relatively large quantity of strong sulphuretted hydrogen water.

If the fluid contained no hydrochloric acid or metallic chloride, the sulphide of lead is pure. After it has been filtered off, washed with cold water and dried, it is transferred, together with the filter-ash, to a porcelain crucible, a little sulphur added, and ignited in hydrogen at gentle redness till its weight is constant. It should always be allowed to cool in a current of the gas, before being weighed. As regards the apparatus, see § 108, 2, fig. 79. For the properties of the residue, see § 83, *f*. The results are satisfactory (H. Rose). The heat of the ignition must not be too low, or the residue will contain too much sulphur, nor too high, or the sulphide of lead will begin to volatilize, and disulphide of lead will also be formed with loss of sulphuretted hydrogen. Drying the precipitate at 100° cannot be recommended (§ 83, *f*). If the fluid, on the contrary, contained hydrochloric acid or a metallic chloride, the sulphide of lead contains chloride which cannot be removed even by boiling the precipitate with sulphide of ammonium. If the precipitate were treated as above, we should obtain a tolerably pure sulphide, but not without loss from volatilization of chloride. A precipitate of this kind must therefore be decomposed with strong hydrochloric acid, the solution evaporated to dryness, the residue dissolved by heating with a concentrated solution of acetate of soda, and this solution diluted and poured with stirring into excess of strong sulphuretted hydrogen water. Or the chloride of lead obtained may be evaporated, heated to 200°, and weighed as such (FINKENER*).

3. *Determination as Sulphate.*

a. By Precipitation.

a. Mix the solution (which should not be over dilute) with moderately dilute pure sulphuric acid slightly in excess, and add to the mixture double its volume of spirit of wine; wait a few hours, to allow the precipitate to subside; filter, wash the precipitate with spirit of wine, dry, and ignite after the method described in § 53. Though a careful operator may use a platinum crucible, still a thin porcelain crucible is preferable. See also the remarks, 1, *a.*

β. In cases where the addition of spirit of wine is inadmissible, a greater excess of sulphuric acid must be used, and the precipitate, which is allowed some time to subside, filtered, and washed first with water acidulated with a few drops of sulphuric acid, then repeatedly with spirit of wine. The remainder of the process is conducted as in *a.*

If the fluid contained nitric acid, whether spirit of wine is used or not, it is advisable to evaporate on the water-bath after the addition of the sulphuric acid, till the nitric acid has escaped, otherwise the precipitation will not be complete. If the fluid contained hydrochloric acid or a metallic chloride, chloride of lead is thrown down with the sulphate. In this case you must either evaporate the fluid with excess of sulphuric acid and heat the residue till sulphuric acid fumes escape to drive off the hydrochloric acid, or you must treat the precipitate and filter-ash in the crucible with concentrated sulphuric acid, evaporate and ignite to convert it into pure sulphate of lead (FINKENER†).

For the properties of the precipitate, see § 83. The method *a* gives accurate results; those obtained by *β* are less exact (a little too low), but still however satisfactory, if the directions given are adhered to. If, on the contrary, a proper excess of sulphuric acid is not added, in the presence, for instance, of ammoniacal salts, the lead is not completely precipitated, and if pure water is used for washing, decided traces of the precipitate are dissolved.

b. By Evaporation.

a. Put the substance into a weighed dish, dissolve in dilute nitric acid, add moderately dilute pure sulphuric acid slightly in excess, and evaporate at a gentle heat; at last high over the lamp, until the excess of sulphuric acid is completely expelled. In the absence of organic substances, the evaporation may be effected without fear in a platinum dish; but if organic substances are present, a light porcelain dish is preferable. With due care in the process of evaporation, the results are perfectly accurate.

β. Organic compounds of lead are converted into the sulphate by treating them in a porcelain crucible, with pure concentrated sulphuric acid in excess, evaporating cautiously in the well-covered crucible, until the excess of sulphuric acid is completely expelled, and igniting the residue. Should the latter not look perfectly white, it must be moistened once more with sulphuric acid, and the operation repeated. The method gives, when conducted with great care, accurate results; a trifling loss is, however, usually incurred, the escaping sulphurous acid and carbonic acid gases being liable to carry away traces of the salt.

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* Handb. der anal. Chem. von H. ROSE, 6 Aufl. von FINKENER, 932.

† *Ib.* 933.

4. *Determination as Chromate of Lead.*

If the solution is not already distinctly acid render it so with acetic acid, then add bichromate of potassa in excess, and, if free nitric acid is present, add acetate of soda in sufficient quantity to replace the free nitric acid by free acetic acid; let the precipitate subside at a gentle heat, and collect on a weighed filter dried at 100°, wash with water, dry at 100°, and weigh. The precipitate may also be ignited according to § 53, but in this case care must be taken that hardly any of the salt remains adhering to the paper, and that the heat is not too high. For the properties of the precipitate, see § 93, 2. The results are accurate. (Expt. No. 68.)

5. *Determination as Chloride of Lead.*

Mix the solution with hydrochloric acid in excess, concentrate strongly in the water-bath, treat the residue with absolute alcohol mixed with a little ether, let the precipitate subside, filter and wash with alcohol mixed with ether. The chloride of lead may be either dried at 100° (being collected on a weighed filter) or treated according to § 53. In the latter case a porcelain crucible is used, and care is taken that the least possible amount of the salt remains adhering to the filter and that the heat is not raised beyond 200°. This method is had recourse to in certain separations.

6. *Determination as Oxide of Lead + Lead.*

Heat from one to two grm. of the organic compound of lead in a small weighed porcelain dish very gently, taking care to make the heat act first upon the rim of the dish, so that the ensuing decomposition may begin on one side, and proceed slowly. When the whole mass is perfectly decomposed, increase the heat a little, and continue until no more glowing particles are perceptible, and the residue forms a mixture of oxide of lead with globules of metallic lead, free from carbon. Weigh the residue; then heat it with acetic until the oxide is completely dissolved, which does not take long; pour off the solution now from the metallic lead, and wash the latter by repeated decantation; remove the last traces of water by heat, and weigh the residuary metallic lead. By subtracting the weight of the metal from that of the original residue, you will find the quantity of oxide of lead which was present in that residue; and by calculating the proportion of metal contained in the oxide, and adding the resulting number to the weight of the metallic lead, you will obtain the total amount of that metal originally present in the analysed compound. This method is very convenient, and, if properly and carefully executed, gives very accurate results. The operator must take care to conduct the decomposition of the organic compound very slowly, since the rapid combustion of its carbon and hydrogen, at the expense of the oxygen of the oxide of lead, would produce so high a temperature as to volatilize a portion of the lead in visible fumes. If the residue is not perfectly free from carbon—which will always be detected in heating it with acetic acid—this will tend to give a higher number.

This method was originally introduced by **Berzelius**. **Dulk** has recommended the following modification:—The compound to be analysed is gently heated, in a covered porcelain crucible, until the organic substance is completely carbonized; the lid is then removed, and the mass stirred with a piece of iron wire. Upon this, the mass begins to ignite, and a mixture of oxide of lead with metallic lead results, which may still contain unconsumed carbon. A few pieces of recently fused nitrate of ammonia are now thrown into the crucible, which has previously been removed from the flame, and the lid is again put on. The salt fuses, oxidizes the lead, and converts it partly into nitrate. The crucible is now exposed to a red heat, until no more fumes of hyponitric acid escape. The residuary oxide is then weighed. This method possesses the advantage of insuring the complete combustion of the whole of the carbon; it saves also some trouble in weighing and calculating. The results are quite satisfactory.

7. *Determination as Lead.*

a. The following method serves for the analysis of the oxide and most compounds of lead, such as the sulphate and phosphate, but not the chromate. Sulphide of lead is decomposed with difficulty. Fuse the substance with four or five times its weight of cyanide of potassium, prepared by **Liebig**'s process, in a covered and well glazed porcelain crucible. After cooling treat with water, decant the fluid rapidly from the reduced lead, wash with water, then with dilute, and finally with strong spirit, dry and weigh. Occasionally we get a single globule of lead, but usually several small globules, mixed with a metallic powder. After weighing dissolve the lead in warm dilute nitric acid. If a residue remains (portions of the glaze of the crucible) determine its weight and deduct it (H. **Rose***).

b. From soluble and insoluble salts of lead, especially from the chloride and sulphate, the lead may be separated by zinc or cadmium. To this end the substance is warmed with water and some hydrochloric acid in a water-bath, and a smooth piece of zinc or cadmium (soluble in hydrochloric acid without residue) is put into the fluid. The reduction commences at once, the lead deposited on the zinc is removed from time to time with a rod, and more hydrochloric acid is added as necessary. If the zinc, after having been freed from lead, remains bright for some time, and if a small portion of the solution gives no precipitate or coloration with sulphuretted hydrogen, the precipitation is complete. The zinc or cadmium is removed, the fluid is poured off, and the spongy lead is washed by decantation rapidly and thoroughly with spring water; distilled water would dissolve traces of lead. To prevent the spring water from precipitating the zinc or cadmium add to it some tincture of logwood, and then very dilute sulphuric acid, till the red color has just turned yellow. The spongy lead cannot be dried without the formation of hydrated oxide, hence you may either dry at 150° to 200°, weigh the mixture of lead and oxide, determine the latter volumetrically according to 8, *c*, and find the amount of oxygen which has to be deducted from the weighed mixture; or you may dissolve in nitric acid, and determine the lead as sulphate according to 3, *b* (**Stolba**†).

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* Pogg. Annal. 91, 104.

† Journ. f. prakt. Chem. 101, 150; Zeitschr. f. anal. Chem. 7, 102.

8. *Determination of Lead by Volumetric Analysis.*

Although there is no lack of proposed methods for the volumetric estimation of lead, we are still without a really good method for practical purposes, that is, a method which can be generally employed, and which is at the same time simple and exact. For the present, therefore, in almost all cases the gravimetric determination of lead is to be preferred to the volumetric. On my own part, at least, I cannot see that it is easier or any better, when one has the precipitate washed, to subject it to a volumetric process—whereby the accuracy is necessarily diminished—instead of igniting it gently and weighing. For this reason, the better volumetric methods will be but briefly described, the rest being altogether omitted.

a. The solution of the neutral lead salt must be free from alkaline salts, more especially from ammonia salts. It is precipitated with oxalic acid (not with oxalate of ammonia), the well-washed precipitate is dissolved in nitric acid, sulphuric acid added, and the oxalic acid in the solution determined by permanganate of potassa (§ 137) HEMPEL.

b. H. SCHWARZ's method*. To the nitric acid solution add ammonia or carbonate of soda, as long as the precipitate redissolves on shaking, mix with acetate of soda in not too small quantity, and then run in from a burette a solution of bichromate of potash (containing 14·761 grm. in the litre) till the precipitate begins to settle rapidly. Now place on a porcelain plate a number of drops of a solution of neutral nitrate of silver, and proceed with the addition of the chromate, two or three drops at a time, stirring carefully after each addition. When the precipitate has settled tolerably clear, which takes only a few seconds, remove a drop of the supernatant liquid and mix it with one of the drops of silver on the plate. A small excess of chromate gives at once a distinct red coloration; the precipitated chromate of lead does not act on the silver solution, but remains suspended in the drop. The number of c.c. of solution of chromate used (*minus* ·1 which SCHWARZ deducts for the excess) multiplied by ·0207 = the quantity of lead. If the fluid appear yellow before the reaction with the silver salt occurs, acetate of soda is wanting. In such a case first add more acetate of soda, then 1 c.c. of a solution containing ·0207 lead in 1 c.c., complete the process in the usual way, and deduct 1 c.c. from the quantity of chromate used on account of the extra lead added. Any iron present must be in the form of sesquioxide; metals whose chromates are insoluble, must be removed before the method can be employed.

c. The lead is precipitated according to 1, *a*, the carbonate, (its composition is a matter of indifference in the present case) is washed, dissolved in a measured quantity of normal nitric acid (§ 215), and a neutral solution of sulphate of soda added, whereby sulphate of lead is precipitated and an equivalent quantity of nitrate of soda formed. If the nitric acid still free is now determined with normal alkali, we shall find the quantity of acid that has been neutralized by means of the lead, each 1 c.c. of normal nitric acid that has been so neutralized = ·1035 lead. You may also determine the free nitric acid by adding normal carbonate of soda (53·04 of the anhydrous salt in 1 litre) till, the vessel being on a black surface, a permanent turbidity is visible. Results good (F. MOHR†).

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* Dingl. polyt. Journ. 169, 284.

† His Lehrbuch der Titrirmethode, 3 Aufl. 115.

§ 117.

3. SUBOXIDE OF MERCURY.

a. Solution.

Suboxide of mercury and its compounds may generally be dissolved by means of dilute nitric acid, but without application of heat if conversion of any of the suboxide into oxide is to be avoided. If all that is required is to dissolve the mercury, the easiest way is to warm the substance for some time with nitric acid, then add hydrochloric acid, drop by drop, and continue the application of a moderate heat until a perfectly clear solution is produced, which now contains all the mercury as oxide and chloride. Heating the solution to boiling, or evaporating, must be carefully avoided, as otherwise chloride of mercury may escape with the steam.

b. Determination.

If it is impracticable to produce a solution of the suboxide or its compounds perfectly free from oxide, and it becomes accordingly necessary to convert the mercury completely into oxide, the latter is determined as directed § 118. But if a solution of suboxide has been obtained, quite free from oxide, the determination of the suboxide may be based upon the insolubility of subchloride of mercury, and effected either gravimetrically or volumetrically. The process of determining mercury, described § 118, 1, *a*, may, of course, be applied equally well in the case of compounds of suboxide of mercury.

1. *Determination as Subchloride of Mercury.*

Mix the cold highly dilute solution with solution of chloride of sodium, as long as a precipitate forms; let the precipitate subside, collect on a weighed filter, dry at 100°, and weigh. For the properties of the precipitate, see § 84. Results accurate. If the solution of suboxide of mercury contains much free nitric acid, the greater part of this should be neutralized with carbonate of soda before adding the chloride of sodium.

2. *Volumetric Methods.*

Several methods have been proposed under this head: the following are those which are most worthy of recommendation:—

a. Mix the cold solution with decinormal solution of chloride of sodium (§ 141, *b*, *a*), until this no longer produces a precipitate, and is accordingly present in excess; filter and wash thoroughly, taking care, however, to limit the quantity of water used; add a few drops of solution of chromate of po assa, then pure carbonate of soda, sufficient to impart a light yellow tint to the fluid, and determine by means of solution of nitrate of silver (§ 141, *b*, *a*) the quantity of chloride of sodium in solution, consequently the quantity which has been added in excess; this shows, of course, also the amount of chloride of sodium consumed in effecting the precipitation. One equivalent of Hg_2O is reckoned for every equivalent of NaCl, consequently for every c.c. of the decinormal solution of chloride of sodium, ·0208 grm. of suboxide of mercury. As filtering and washing form indispensable parts of the process, this method affords no great advantage over the gravimetric;

however, the results are accurate (FR. MOHR[*]). The two methods, 1 and 2, *a*, may also be advantageously combined.

b. Precipitate the solution of suboxide of mercury,[†] according to 1, with chloride of sodium in a stoppered bottle, allow to subside, filter, wash, push a hole through the bottom of the filter, and rinse the precipitate into the bottle, which usually has some of the washed subchloride adhering to its inside. Add a sufficient quantity of solution of iodide of potassium, together with standard iodine solution (to 1 grm. Hg_2Cl about 2·5 grm. KI and 100 c.c. $\frac{1}{10}$ normal iodine solution[‡]), insert the stopper, and shake till the precipitate has entirely dissolved $[Hg_2Cl + 3KI + I = 2(HgI,KI) + KCl]$. As iodine is in excess, the solution appears brown. If any iodide of mercury separates add iodide of potassium to redissolve it. Now add from a burette solution of hyposulphite of soda—corresponding to decinormal iodine solution—till the fluid is decolorized and appears like water, transfer to a measuring flask, rinse and fill up to the mark, shake, take out an aliquot part, add starch paste to it, and determine the excess of hyposulphite of soda with $\frac{1}{10}$ iodine solution. After multiplying by the proper number, add the c.c. originally employed, subtract the c.c. of hyposulphite used, and reckon the quantity of mercury from the remainder. 1 eq. iodine = 1 eq. Hg_2Cl. Results good (HEMPEL[§]).

§ 118.

4. OXIDE OF MERCURY.

a. Solution.

Oxide of mercury, and those of its compounds which are insoluble in water, are dissolved, according to circumstances, in hydrochloric acid or in nitric acid. Sulphide of mercury is heated with hydrochloric acid, and nitric acid or chlorate of potassa added until complete solution ensues; or it is suspended in dilute potassa, gently warmed, and chlorine gas passed through (H. ROSE). When a solution of chloride of mercury is evaporated on the water-bath, chloride of mercury escapes with the aqueous vapor. This circumstance must not be lost sight of in effecting the solution of compounds of mercury. It is from this cause that the method proposed by VOHL[||] gives quite inaccurate results. FR. MOHR[¶] too and R. RIETH[**] have not paid enough regard to this source of error.

b. Determination.

Mercury may be weighed in the *metallic state*, or as *subchloride*, *sulphide*, or *oxide* (§ 84); in separations it is sometimes determined as loss on ignition. It may also be estimated volumetrically.

The first three methods may be used in almost all cases; the determination as oxide, on the contrary, is only possible in compounds of the oxide or suboxide with nitric acid. The methods by which the mercury is determined as subchloride or sulphide are to be preferred before those in which it is separated in the metallic form. The volumetric methods are only of very limited application.

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[*] Lehrbuch der Titrirmethode, 3 Aufl. 395.

[†] If oxide of mercury is also present, see § 118, 2.

[‡] See § 146, 2.

[§] Annal. d. Chem. u. Pharm. 110, 176.

[||] *Ib.* 94, 220.

[¶] His Lehrbuch der Titrirmethode, 3 Aufl. 208.

[**] His Volumetrie, 225.

1. *Determination as Metallic Mercury.*

a. In the Dry Way.

The process is conducted in the apparatus illustrated by fig. 84.

Take a tube 45 cm. long, and about 12 mm. wide made of difficultly fusible glass, and sealed at one end. First put into the tube a layer 6 cm. long of a mixture of bicarbonate of soda and powdered chalk, then a layer of quick-lime, these two will occupy the space from *a* to *b*. Then add the intimate mixture of the substance with an excess of quick-lime (*b*-*c*), then the lime-rinsings of the mortar (*c*-*d*), then a layer of quick-lime (*d*-*e*) and lastly, a loose stopper of asbestus (*e*-*f*). The anterior end of the tube is then drawn out, and bent at a somewhat obtuse angle. The manipulations in the processes of mixing and filling being the same as in organic analysis, they will be found described in detail in the chapter on that subject.

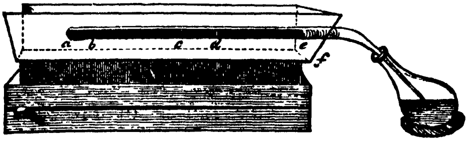

Fig. 84.

A few gentle taps upon the table are sufficient to shake the contents of the tube down so as to leave a free passage through the whole length of the tube. The tube, so prepared and arranged, is now placed in a combustion furnace, the point being inserted into a flask containing water, the surface of which it should just touch, so that the opening may be just closed.

The tube is now surrounded with red-hot charcoal, in the same way as in organic analysis, proceeding slowly from *e* to *a*, the last traces of mercurial vapor being expelled by heating the mixture at the sealed end of the tube. Whilst the tube still remains in a state of intense ignition, the neck is cut off at *f*, and carefully and completely rinsed into the receiving flask, by means of a washing-bottle. The small globules of mercury which have distilled over are united into a large one, by agitating the flask, and, after the lapse of some time, the perfectly clear water is decanted, and the mercury poured into a weighed porcelain crucible, where the greater portion of the water still adhering to it is removed with blotting-paper. The mercury is then finally dried under a bell-jar, over concentrated sulphuric acid, until the weight remains constant. Heat must not be applied. For the properties of the metal, see § 84. In the case of sulphides, in order to avoid the presence of vapor of water in the tube which would give rise to the formation of sulphuretted hydrogen, the mixture of bicarbonate of soda and chalk is replaced by magnesite. Iodide of mercury cannot be completely decomposed by lime. To analyse this in the dry way, substitute finely divided metallic copper for the lime (H. Rose*). The accuracy of the results is entirely dependent on the care bestowed. The most highly accurate results are, however, obtained by the application of the somewhat more complicated modification adopted by **Erdmann** and **Marchand** for the determination of the atomic weight of mercury and of sulphur. For the details of this modified process, I refer to the original essay,* simply remarking here, that the distillation is conducted in a combustion tube in a current of carbonic acid gas, and that the distillate is received in a weighed bulb apparatus with the outer end filled with gold-leaf, to insure the condensation of every trace of mercury vapor. This way of receiving and condensing may be employed also in the analysis of amalgams (KÖNIG†).

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* Pogg. Annal. 110, 546.

b. In the Wet Way.

The precipitating flask must be absolutely clean, and had best be purified with hot potash. The solution, free from nitric acid, and mixed with hydrochloric acid, is precipitated, with an excess of a fresh solution of protochloride of tin, containing hydrochloric acid; the mixture is boiled for a short time, and the flask is loosely closed. After cooling and standing for some time, the perfectly clear supernatant fluid is decanted from the metallic mercury, which, under favorable circumstances, will be found united into one globule; if this is the case, the globule of mercury may be washed at once by decantation, first with water acidulated with hydrochloric acid, and finally with pure water; it is dried as in *a.*

If, on the other hand, the particles of the mercury have not united, their union into one globule may as a rule be readily effected by boiling a short time with some moderately dilute hydrochloric acid mixed with a few drops of protochloride of tin (having, of course, previously removed by decantation the supernatant clear fluid). For the properties of metallic mercury, see § 84.

Instead of protochloride of tin, other reducing agents may be used, especially phosphorous acid at a boiling temperature. This method gives accurate results only when conducted with the greatest care. In general a little mercury is lost.

2. *Determination as Subchloride of Mercury.*

a. After H. ROSE.‡ If nitric acid is present, dilute considerably before proceeding. Mix with hydrochloric acid and excess of phosphorous acid (obtained by the deliquescence of phosphorus in moist air), allow to stand 12 hours in the cold or at a very gentle heat (at all events under 60°), collect the mercury, now completely separated as subchloride, on a weighed filter, wash with hot water, dry at 100°, and weigh. Results perfectly satisfactory.

3. *Determination as Sulphide of Mercury.*

The solution is sufficiently diluted, acidulated with hydrochloric acid, and precipitated with clear saturated sulphuretted hydrogen water (or in the case of large quantities, by passing the gas);—filter after allowing the precipitate a short time to deposit, wash quickly with cold water, dry at 100°, and weigh. Results very satisfactory.

If from any cause (*e.g.* presence of sesquioxide of iron, free chlorine, or the like) the precipitate should contain free sulphur, the filter is spread out on a glass plate, the precipitate removed to a porcelain dish by the aid of a jet from the wash-bottle, and warmed for some time with a moderately strong solution of sulphite of soda. The filter having been in the meanwhile somewhat dried on the glass plate, is replaced in the funnel, the supernatant fluid is poured on to it, the treatment with sulphite of soda is repeated, and the precipitate (now free from sulphur), is finally collected on the filter, washed, dried, and weighed. Results good (J. Löwe*).

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* Journ. f. prakt. Chem. 31, 385; also Pharm. Centralbl. 1844, 354.

† Journ. f. prakt. Chem. 70, 64.

‡ Pogg. Annal. 110, 529.

Should the quantity of sulphur mixed with the precipitate be not very large, it may be removed also as follows: the precipitate is first washed with water, and fully dried, then washed repeatedly with bisulphide of carbon, till a few drops of the washings evaporate on a watch-glass without leaving a residue. Test the bisulphide of carbon to see if it gives any residue when evaporated.

Properties of the sulphide of mercury § 84.

4. *Determination as Oxide.*

In the salts of the oxides of mercury, with nitrogen acids, the metal may be very conveniently determined in the form of oxide (Marignac†). For this purpose, the salt is heated in a bulb-tube, of which the one end, drawn out to a point, dips under water, the other end being connected with a gasometer, by means of which dry air is transmitted through the tube, as long as the application of heat is continued. In this way complete decomposition of the salt is readily effected, without reaching the temperature at which the oxide itself would be decomposed.

5. *Volumetric Methods.*

a. The mercury is precipitated as subchloride, according to 2, and the washed precipitate treated as in § 117, 2, *b.*

b. After Liebig.‡ This method is based upon the circumstance that phosphate of soda precipitates mercury from solutions of the nitrate, but not from solutions of the chloride, in the form of a flocculent white precipitate of phosphate, which speedily becomes crystalline; and that chloride of sodium, therefore, readily redissolves this precipitate (as long as it remains amorphous), phosphate of soda and chloride of mercury being formed. Consequently, if we know the quantity of chloride of sodium required to redissolve the precipitate, we learn from this also the quantity of the mercury; since every equivalent of chloride of sodium dissolves an equivalent of oxide of mercury (in the form of phosphate).

α. Solution of Chloride of Sodium: The decinormal solution of chloride of sodium may be used. Every c.c. of this, containing ·00585 grm. NaCl, corresponds accordingly to ·01080 of HgO.

β. Preparation of the Solution of Oxide of Mercury: According to Liebig, this solution—which must, of course, be perfectly free from compounds of chlorine, iodine, and bromine, and in which all the mercury must be present in the state of oxide—should contain no more than about ·2 grm. oxide of mercury in 10 c.c. Accordingly, if a preliminary experiment shows it to have a higher degree of concentration it is diluted to about this strength. The solution must, moreover, contain no foreign metals, nor too much free acid: the addition of from 3 to 4 c.c. of a saturated solution of phosphate of soda to 10 c.c.

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* Journ. f. prakt. Chem. 77, 73.

† Jahresber. von Liebig u. Kopp, 1849, 594.

‡ Annal. d. Chem. u. Pharm. 85, 307.

of the solution, must remove all acid reaction. If too much acid is present, carbonate of soda must be added until basic salt precipitates, which latter is then redissolved by addition of one or two drops of nitric acid.

γ. *Performance of the Analytical Process:* There are two different methods recommended, both of which it is best to apply, as the results obtained by the former are somewhat too high, those by the latter a little too low. The results being combined, the two errors cancel each other.

Method 1. Measure off into a beaker 10 c.c. of the solution of mercury, add 3 or 4 c.c. of a saturated solution of phosphate of soda, and then immediately, before the precipitate has had time to become crystalline, solution of chloride of sodium, until the precipitate is just redissolved; the last portions of the solution of chloride of sodium must be added very cautiously to avoid addition in excess.

Supposing you have used 20·5 c.c. of solution of chloride of sodium, now—

Method 2. Measure off 20·5 c.c. of the same solution of chloride of sodium, add to this 3 or 4 c.c. of solution of phosphate of soda, and then solution of oxide of mercury from a burette, until a permanent precipitate just begins to form. Supposing this has taken 10·25 c.c. of solution of mercury, then 20·5 + 20·5 = 41 c.c. of solution of chloride of sodium have been consumed to 10 + 10·25 = 20·25 c.c. of solution of oxide of mercury; now 1 c.c. of the solution of chloride of sodium corresponds to ·01080 grm. oxide of mercury, therefore 41 c.c. correspond to ·4428 grm. oxide of mercury, which quantity is consequently contained in 20·25 c.c. of the analysed solution.

Liebig has proved by numerous experiments that this course of proceeding gives very nearly accurate results; he obtained, for instance, ·1878 grm. instead of ·1870 grm., ·174 grm. instead of ·1748 grm., ·1608 grm. instead of ·1604 grm., &c. But the method is susceptible only of very limited application; for which reason I omit giving a description of Fr. Mohr's modification of the process, which consists in the substitution of ferricyanide of potassium for phosphate of soda.*

c. As regards Personne's method,† which depends on the addition of chloride of mercury to standard solution of iodide of potassium, till permanent separation of iodide of mercury begins, see my remarks, Zeitschr. f. Anal. Chem. 2, 381.

§ 119.

5. Oxide of Copper.

a. Solution.

Many of the compounds of oxide of copper dissolve in water. Metallic copper is best dissolved in nitric acid. Oxide of copper, and those of its salts which are insoluble in water, may be dissolved in nitric, hydrochloric, or sulphuric acid. Sulphide of copper is treated with fuming nitric acid, or it is heated with moderately dilute nitric acid, until the separated sulphur exhibits a pure yellow tint; addition of a little hydrochloric acid or chlorate of potassa greatly promotes the action of the dilute acid.

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* See his Lehrbuch der Titrirmethode, 3 Aufl. 396.

† Journ. de Pharm. et de Chim. 43, 477.

b. Determination.

Copper may be weighed in the form of *oxide*, or in the *metallic state*, or as *subsulphide* (§ 85). Into the form of oxide it is converted by precipitation, or ignition, sometimes with previous precipitation as sulphide. The determination as subsulphide is preceded usually by precipitation either as sulphide or as subsulphocyanide. Copper may be determined also by various volumetric and indirect methods.

We may convert into

1. OXIDE OF COPPER:

a. By direct Precipitation as oxide: All salts of oxide of copper soluble in water, and also those insoluble salts, the acids of which may be removed upon solution in nitric acid, provided no non-volatile organic substances be present.

b. By Precipitation, preceded by Ignition of the compound: Such of the salts enumerated under *a* as contain a non-volatile organic substance, thus more particularly salts of copper with non-volatile organic acids.

c. By Ignition: Salts of copper with oxygen acids that are readily volatile or decomposable at a high temperature (carbonate of copper, nitrate of copper).

2. METALLIC COPPER: Oxide of copper in all solutions free from other metals precipitable by zinc or the galvanic current, also the oxides of copper.

3. SUBSULPHIDE OF COPPER: Oxide of copper in all cases in which no other metals are present that are precipitable by sulphuretted hydrogen, or sulphocyanide of potassium.

Of the several methods of effecting the estimation of copper, No. 3 is particularly to be recommended for use in laboratories; method 2 is also very convenient, and well adapted for assaying. Of the volumetric methods, one is suited for technical purposes, the other for the estimation of small quantities of copper. For technical purposes there are besides, also several colorimetric methods, proposed by HEINE, VON HUBERT, JACQUELAIN, A. MÜLLER, and others, which are, all of them, based upon the comparison of an ammoniacal solution of oxide of copper, of unknown strength, with others of known strength.*

LEVOL'S indirect method of estimating copper, which is based upon the diminution of weight suffered by a strip of copper when digested in a close stoppered flask with ammoniacal solution of copper till decolorization is effected, takes too much time, and is apt to give false results (PHILLIPS,† ERDMANN‡). The latter remark applies also to the indirect method proposed by RUNGE, which consists in boiling the solution of copper, free from nitric acid and sesquioxide of iron, in presence of some free hydrochloric acid, in a flask, with a weighed strip of copper, and, after decolorization of the fluid, determining the loss of weight suffered by the copper.

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* This subject hardly comes within the scope of the present work. I therefore refer to AL. MÜLLER, das Complementärcolorimeter, Chemnitz, 1854; BODEMANN'S Probirkunst von KERL, 222; also to DEHMS, Zeitschr. f. anal. Chem. 3, 218, and GUSTAV BISCHOF, jun. *Ib.* 6, 459.

† Annal. d. Chem. u. Pharm. 81, 208.

‡ Journ. f. prakt. Chem. 75, 211.

1. *Determination as Oxide of Copper.*

a. By direct Precipitation as Oxide.

Heat the rather dilute *neutral* or *acid* solution in a platinum or porcelain dish, to incipient ebullition, add a somewhat dilute solution of pure soda or potassa until the formation of a precipitate ceases, and keep the mixture a few minutes longer at a temperature near boiling. Allow to subside, filter, wash by decantation twice or thrice, boiling up each time, then collect it on the filter, wash thoroughly with hot water, dry, and ignite in a porcelain or platinum crucible, as directed § 53. Do not use the blowpipe. After ignition, and having added the ash of the filter, let the crucible cool in the desiccator, and weigh. The action of reducing gases must be carefully guarded against in the process of ignition.

It will sometimes happen, though mostly from want of proper attention to the directions here given, that particles of the oxide of copper adhere so tenaciously to the dish as to be mechanically irremovable. In a case of this kind, after washing the dish thoroughly, dissolve the adhering particles with a few drops of nitric acid, and evaporate the solution over the principal mass of the precipitated oxide, before you proceed to ignite the latter. Should the solution be rather copious, it must first be concentrated by evaporation, until only *very little* of it is left. For the properties of the precipitate, see § 85.

With proper attention to the directions here given, the results obtained by this method are quite accurate, otherwise they may be either too high or too low. Thus, if the solution be not sufficiently dilute, the precipitant will fail to throw down the whole of the oxide of copper; or, if the precipitate be not thoroughly washed with hot water, it will retain a portion of the alkali; or, if the ignited precipitate be allowed to stand exposed to the air, before it is weighed, an increase of weight will be the result; and so, on the other hand, a diminution of weight, if the oxide be ignited with the filter or under the influence of reducing gases, as thereby suboxide would be formed. Should a portion of the oxide have suffered reduction, it must be reoxidized by moistening with nitric acid, evaporating cautiously to dryness, and exposing the residue to a gentle heat, increasing this gradually to a high degree of intensity.

Let it be an invariable rule to test the filtrate for copper with sulphuretted hydrogen water. If, notwithstanding the strictest compliance with the directions here given, the addition of this reagent produces a precipitate, or imparts a brown tint to the fluid, this is to be attributed to the presence of organic matter; in that case, concentrate the filtrate and wash-water by evaporation, acidify, precipitate with sulphuretted hydrogen water, filter, incinerate the filter, heat with nitric acid, dilute, filter, concentrate, precipitate with soda, and filter the oxide obtained to the main quantity.

Never neglect to test the oxide of copper after weighing for alkali or alkaline salt by boiling it with water. If either is present, the oxide must be exhausted with hot water, and then reignited and reweighed. Finally, dissolve the oxide in hydrochloric acid to detect and if necessary estimate any silicic acid it may contain.

In default of sufficiently pure potash or soda, the carbonate may be used, but the solution must not contain more than 1 grm. copper in the litre; the alkaline carbonate must only be added slightly in excess, and the mixture must be boiled for half an hour. The bluish-green precipitate will then turn dark brown and granular, and may be easily washed (GIBBS*).

From *ammoniacal* solutions also, oxide of copper may be precipitated by soda or potassa. In the main, the process is conducted as above. After precipitation the mixture is heated, until the supernatant fluid has become perfectly colorless; the fluid is then filtered off with the greatest possible expedition. If allowed to cool with the precipitate in it a small portion of the latter would redissolve.

b. By Precipitation as Oxide, preceded by Ignition of the Substance.

Heat the substance in a porcelain crucible, until the organic matter present is totally destroyed; dissolve the residue in dilute nitric acid, filter if necessary, and treat the clear solution as directed in *a.*

c. By Ignition.

The salt is put into a platinum or porcelain crucible, and exposed to a very gentle heat, which is gradually increased to intense redness; the residue is then weighed. As nitrate of copper spirts strongly when ignited, it is always advisable to put it into a small covered platinum crucible, and to place the latter in a large one, also covered. With proper care, the results are accurate. Copper salts with organic acids may also be converted into oxide by simple ignition. To this end, the residue first obtained, which contains suboxide, is completely oxidized by ignition with oxide of mercury (which leaves no residue on ignition), or with less advantage, by repeated moistening with nitric acid, and ignition. A loss of substance is generally incurred by the use of nitric acid from the difficulty of avoiding spirting.

2. *Determination as Metallic Copper.*

a. By Precipitation with zinc or cadmium†.

Introduce the solution of copper, after having, if required, first freed it from nitric acid, by evaporation with hydrochloric acid or sulphuric acid, into a weighed platinum dish; dilute, if necessary with some water, throw in a piece of zinc (soluble in hydrochloric acid without residue) and add, if necessary, hydrochloric acid in sufficient quantity to produce a moderate evolution of hydrogen. If, on the other hand, this evolution should be too brisk, owing to too large excess of acid, add a little water. Cover the dish with a watch-glass, which is afterwards rinsed into the dish with the aid of a washing-bottle. The separation of the copper begins immediately; a large proportion of it is deposited on the platinum in form of a solid coating; another portion separates, more particularly from concentrated solutions, in the form of red spongy masses. Application of heat, though it promotes the reaction, is not absolutely necessary; but there must always be sufficient free acid present to keep up the evolution of hydrogen. After the lapse of about an hour or two, the whole of the copper has separated. To make sure of this, test a small portion of the supernatant fluid with sulphuretted hydrogen water; if this fails to impart a brown tint to it, you may safely assume that the precipitation of the copper is complete. Ascertain now, also, whether the zinc is entirely dissolved, by feeling about for any hard lumps with a glass rod, and observing whether renewed evolution of hydrogen will take place upon addition of some hydrochloric acid. If the results are satisfactory in this respect also, press the copper together with the glass rod, decant the clear fluid, which is an easy operation, pour, without loss of time, boiling water into the dish, decant again, and repeat this operation until the washings are quite free from hydrochloric acid. Decant the water now as far as practicable, rinse the dish with strong alcohol, dry at 100°, let it cool, and weigh. If you have no platinum dish, the precipitation may be effected also in a porcelain crucible or glass dish; but it will, in that case, take a longer time; and the whole of the copper will be obtained in loose masses, and not firmly adhering to the sides of the crucible or dish, as in the case of precipitation in platinum vessels.

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* Zeitschr. f. anal. Chem. 7, 258.

† The method of precipitating copper by iron or zinc, and weighing it in the metallic form, was proposed long ago; see PFAFF'S Handbuch der analytischen Chemie, Altona, 1822, 2, 269, where the reasons are given for preferring zinc as a precipitant, and sulphuretted hydrogen is recommended as a test for ascertaining whether the precipitation is complete. I mention this with reference to F. MOHR'S paper in the Annal. d. Chem. u. Pharm. 96, 215, and BODEMANN'S Probirkunst von KERL, 220.

The results are very accurate. The direct experiment, No. 69, gave 100·0 and 100·06, instead of 100. FR. MOHR (*loc. cit.*) obtained equally satisfactory results by precipitating in a porcelain crucible.*

Zinc being sometimes difficult to obtain of sufficient purity, cadmium may be used instead; it dissolves with less violence in strongly acid copper solutions. It may be used in the form of rod, in which it usually occurs in commerce (CLASSEN†).

b. By Precipitation with the galvanic current.

This method makes us independent of pure zinc or cadmium, and yields the copper in a compact form, readily washed and determined. It is now largely used in copper works, constant batteries have been employed for it, and the whole process has been organized for use on a large scale by LUCKOW, and adopted by the Mansfeld Ober-Berg- und Hütten-Direction in Eisleben‡. A small electrolytic apparatus without separate battery, for single precipitations, has been described by ULLGREN.§

c. By Ignition in Hydrogen.

The oxides of copper when ignited in a current of pure hydrogen are converted into metallic copper, and may thus be conveniently analysed. Occasionally the oxide obtained by 1, *a* or *b* is reduced either at once, or after weighing; in the latter case the reduction serves as a control.

3. *Determination as Subsulphide of Copper.*

a. By Precipitation as Sulphide.—Precipitate the solution—which is best moderately acid, but should not contain a great excess of nitric acid—according to the quantity of copper present, either by the addition of strong sulphuretted hydrogen water, or by passing the gas. In the absence of nitric acid it is well to heat nearly to boiling while the gas is passing, as this makes the precipitate denser, and it is more easily washed. When the precipitate has fully subsided, and you have made sure that the supernatant fluid is no longer colored or precipitated by strong *sulphuretted hydrogen water*, filter quickly, wash the precipitate without intermission with water containing sulphuretted hydrogen, and dry on the filter with some expedition. Transfer to a weighed porcelain crucible, add the filter-ash and some pure powdered sulphur and ignite strongly in a stream of hydrogen (§ 108, fig. 79). It is advisable to use a gas-blowpipe. The results are very accurate (H. ROSE*).

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* STORER (On the alloys of copper and zinc, Cambridge, 1860, p. 47) says that the precipitated copper retains water, but I have not found this to be the case (See Expt. No. 70).

† Journ. f prakt. Chem. 96, 259.

‡ Zeitschr. f. anal. Chem 8, 23 and 11, 1. Compare also GIBBS, *Ib.* 3, 334, and LECOQ DE BOISBAUDAN, *Ib.* 7, 253.

§ *Ib.* 7, 442.

This method, which was recommended by BERZELIUS, and afterwards by BRUNNER, has only lately received a very practical form, from the apparatus introduced by H. ROSE. I feel great pleasure in recommending it. In my own laboratory it is in frequent use.

If the sulphide of copper is ignited in a covered crucible, from which the lamp and the cover are occasionally removed for a few seconds, it will be converted into a variable mixture of Cu_2S and CuO, in which, however, the percentage of copper is constant (ULRICI†). When the copper is weighed in this form the results are not quite so accurate as when it is weighed as subsulphide.

b. By Precipitation as Subsulphocyanide, after RIVOT.‡—The solution should be as free as possible from nitric acid and free chlorine, and should contain little or no free acid. Add sulphurous or hypophosphorous acid in sufficient quantity, and then solution of sulphocyanide of potassium in the least possible excess. The copper precipitates as white subsulphocyanide. It is filtered after standing some time, washed and dried, mixed with sulphur, ignited in hydrogen in the apparatus mentioned in *a*, and this ignition with sulphur is repeated till the weight is constant. The precipitate may also be collected on a weighed filter, dried at 100°, and then weighed. The experiment, No. 71, conducted in the latter way, gave 99·66 instead of 100. The process yields satisfactory results, but they are always inclined to be a little too low, as the subsulphocyanide is not absolutely insoluble. The loss is larger in the presence of much free acid.

c. Oxide and suboxide of copper, sulphate, and many other salts of copper (but not chloride, bromide, or iodide) may be directly converted into subsulphide, by mixing with sulphur and igniting in hydrogen as in *a* (H. ROSE, *loc. cit.*). The results are thoroughly satisfactory.

4. *Volumetric Methods.*

a. DE HAEN'S METHOD.§

I recommend this method, which was devised in my own laboratory,‖ as more especially applicable in cases where small quantities of copper are to be estimated in an expeditious way. The method is based upon the fact that, when a salt of oxide of copper in solution is mixed with iodide of potassium in excess, subiodide of copper and free iodine are formed, the latter remaining dissolved in the solution of iodide of potassium: $2(CuO,SO_3) + 2KI = Cu_2I + 2(KO,SO_3) + I$. Now, by estimating the iodine by Bunsen's method, or with hyposulphite of soda (§ 146), we learn the quantity of copper, as 1 eq. iodine (126·85) corresponds to 2 eq. copper (63·4). The following is the most convenient way of proceeding. Dissolve the compound of copper in sulphuric acid, best to a neutral solution; a moderate excess of free sulphuric acid, however, does not injuriously affect the process. Dilute the solution, in a measuring flask, to a definite volume; 100 c.c. should contain from 1 to 2 grm. oxide of copper. Introduce now about 10 c.c. of iodide of potassium solution (1 in 10) into a stoppered bottle, add 10 c.c. of the copper solution, mix, allow to stand 10 minutes, and then determine the separated iodine, either with sulphurous acid and iodine (§ 146, 1), or with hyposulphite of soda (§ 146, 2). The copper solution must be free from sesquioxide of iron and other bodies which decompose iodide of potassium, also free nitric acid, and free hydrochloric acid; and the solution must not be allowed to stand too long before titration. With strict attention to these rules, the results are accurate. De Haen obtained, for instance, ·3567 instead of ·3566 of sulphate of copper, 99·89 and 100·1 instead of 100 of metallic copper. Further experiments (No. 72) have convinced me, however, that, though the results attainable by this method are satisfactory, they are not always quite so accurate as would be supposed from the above figures given by De Haen. Acting upon Fr. Mohr's suggestion, I tried to counteract the injurious influence of the presence of nitric acid, by adding to the solution containing nitric acid first ammonia in excess, then hydrochloric acid to slight excess; the result was by no means satisfactory. The reason of this is that a solution of nitrate of ammonia, mixed with some hydrochloric acid, will, even after a short time, begin to liberate iodine from solution of iodide of potassium.

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* Pogg. Annal. 110, 138.

† Journ. f. prakt. Chem. 107, 110.

‡ Compt. Rend. 38, 868; Journ. f. prakt. Chem. 62, 252.

§ Annal. d. Chem. u. Pharm. 91, 237.

‖ BROWN (Quart. Journ. of the Chem. Soc. 10, 65), who published this as a new method in 1857, must have been ignorant of its previous publication in 1854. The little variation, too, of determining the iodine with hyposulphite of soda (according to SCHWARZ) instead of with sulphurous acid (according to BUNSEN), may be found in MOHR'S Lehrbuch der Titrirmethode, 1, 387 (1855). A similar remark applies to RÜMPLER, who described the method, with slight modification, as a new one, in 1868 (Journ. f. prakt. Chem. 105, 193).

b. Method of Parkes;[*] H. Fleck's modification.[†]

This method depends upon the action of cyanide of potassium on ammoniacal solution of copper. The azure blue color disappears, Cu_2Cy,NH_4Cy and KO are formed, while 1 eq. of cyanogen is separated, which, acting on the free ammonia, gives urea, oxalate of urea, cyanide of ammonium and formiate of ammonia (Liebig[‡]). The decomposition is not always the same, the quantity and degree of concentration of the ammonia has a marked influence on it: compare Liebig (*loc. cit.*), also my own experiments (No. 73 *a*), from which it appears that neutral ammonia salts also affect the results. See also Fleck (*loc. cit.*), v. Wolfskron,[§] Steinbeck[||] and Kirpitschow.[¶]

Fleck proposes the following modification:—Instead of caustic ammonia use a solution of sesquicarbonate of ammonia (1 in 10), warm the mixture to about 60°, and in order to render the end-reaction plainer add 2 drops of solution of ferrocyanide of potassium (1 in 20); the blue color of the solution is not altered by this addition, nor is its clearness affected. The value of the cyanide of potassium solution is first determined, by means of copper solution of known strength, and it is then employed on the copper solution to be examined. On dropping the cyanide of potassium into the blue solution warmed to 60°, the odor of cyanogen is plainly perceptible, and the color gradually disappears. As soon as the ammoniacal double salt of copper is destroyed, the solution becomes red from the formation of ferrocyanide of copper, without any precipitate appearing, and with the addition of a final drop of cyanide of potassium this red color in its turn vanishes, so that the fluid now appears quite colorless.

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[*] Mining Journal, 1851

[†] Polytechn. Centralbl. 1859, 1313.

[‡] Annal. d. Chem. u. Pharm. 95, 118.

[§] Zeitschr. f. anal. Chem. 5, 403.

[||] *Ib.* 8, 16.

[¶] Zeitschr. f. Chem. (2) 7, 207.

The method thus modified yields, it is true, better, but still only approximate results.* Where such are good enough, the method is certainly convenient. I have found that the presence of ammonia salts is here also not without influence (Expt. No. 73 *b*); on this account the method seems to be applicable only, if the standardizing of the cyanide of potassium and the actual analysis are performed under very similar circumstances.

On the latter principle STEINBECK's† method depends, which was devised for the estimation of copper in the Mansfeld shales, and received a premium from the Mansfeld Ober-Berg- und Hütten-Direction. The copper is first thrown down in the metallic state from the hydrochloric acid solution by zinc in contact with platinum. It is washed, dissolved in a definite quantity of nitric acid, mixed with a definite quantity of ammonia, and then titrated with cyanide of potassium. The results are not only concordant but also very nearly correct if the cyanide is standardized under the same conditions as it is used. In standardizing, about the same quantity of copper should be employed as will have to be estimated. The strength of the cyanide is 1 c.c. = ·005 grm. copper.

c. Methods which depend on the precipitation of the copper by sulphide of sodium.

PELOUZE supersaturates the neutral or acid solution with ammonia, heats to between 60 and 80°, and adds sulphide of sodium till the blue color disappears. The precipitate which falls at this temperature consists of $5CuS + CuO$. Since the temperature influences the composition of the precipitate, and the disappearance of the blue color is not a particularly sharp end-reaction, FR. MOHR‡ and KÜNZEL§ have modified the method. The former precipitates in the cold (by which sulphide of copper is thrown down) and tests for the first excess of sulphide of sodium with alkaline solution of lead. The latter precipitates at a boiling heat (when the oxysulphide is rapidly deposited) and tests for the complete precipitation of the copper by bringing a drop of the fluid in contact with freshly precipitated sulphide of zinc which should not be colored brown by it. The strength of the sulphide of sodium should be 1 c.c. = about ·01 grm. copper. To standardize it we use a copper solution containing 10 grm. in 1 litre. 20 c.c. of this are taken (= ·2 grm. copper), supersaturated with ammonia, diluted with water, boiled and titrated with sulphide of sodium. The sulphide of zinc required is prepared by dissolving ordinary zinc in hydrochloric acid, adding ammonia in excess and boiling with a little sulphide of sodium, by which any lead in solution is thrown down; the filtrate is then mixed with sulphide of sodium (not quite sufficient to throw down the whole of the zinc); and the mass obtained is spread out over several layers of blotting paper.

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* In six experiments, in which he had purposely added different quantities of carbonate of ammonia, FLECK used for 100 c.c. copper solution, in the minimum 15·2, in the maximum 15·75, in the mean 15·46 c.c. cyanide of potassium solution.

† Zeitschr. f. anal. Chem. 8, 8.

‡ His Lehrbuch der Titrirmethode, 3 Aufl. 429.

§ Journ. f. prakt. Chem. 88, 486, Zeitschr. f. anal. Chem. 2, 373.

According to **Künzel**, with careful manipulation the error does not exceed ·25 per cent.; the method is therefore quite accurate enough for technical purposes.

d. Methods which depend on the reduction of chloride of copper by protochloride of tin.

E. **Mulder*** was the first to use this reaction as the basis of a method for estimating copper, he adopted indigo carmine as the indicator. **Fr. Weil**† found that if enough hydrochloric acid was present, the loss of color of the hot solution indicated the conclusion of the reduction. The latter prepares the solution of protochloride of tin by dissolving 6 grm. tinfoil in 200 c.c. hot hydrochloric acid and diluting to a litre with boiled water. The copper solution, which is used to standardize the tin before each fresh series of determinations, is prepared by dissolving 7·867 grm. powdered sulphate of copper pressed between blotting paper (= 2 grm. copper) to half a litre. Transfer 25 c.c. of the copper solution (= ·1 grm. copper) to a flask holding about 100 c.c., add 5 c.c. concentrated sulphuric acid, heat to gentle boiling, and maintaining at this temperature, add the tin solution till the fluid appears as colorless as distilled water. Now add 5 c.c. hydrochloric acid, and if a slight color is produced remove this by a few drops of the tin solution. If you wish to satisfy yourself that the reaction is actually finished, mix a small portion after cooling with a drop of chloride of mercury. If no visible turbidity is produced, the protochloride of tin is not in excess. You may therefore add still more till a small separation of subchloride of mercury takes place on testing, but then you should deduct ·05 c.c. from the amount of tin solution used. In titrating an unknown solution of copper you proceed in the same way. Any nitric acid that may be present is first removed by evaporating with excess of sulphuric acid. Sesquioxide of iron, if present, is reduced with the chloride of copper. In that case, in a second portion of the solution precipitate the copper by means of zinc and platinum wire in the heat, determine the protoxide of iron obtained with permanganate or chromate of potash (§ 112), and then calculate how much protochloride of tin was required to reduce the sesquioxide of iron; the remainder corresponds to the chloride of copper. Or you may wash the precipitated copper, dissolve it in sulphuric acid and reduce with protochloride of tin. The test analyses communicated by **Weil** are satisfactory.

e. **Schwarz**‡ precipitates the copper as suboxide by heating the solution of the tartrate of copper and potash with grape sugar, filters, washes, warms with sesquichloride of iron and hydrochloric acid, and determines the protochloride of iron with permanganate§. $Cu_2O + Fe_2Cl_3 + HCl = 2CuCl + 2FeCl + HO$.

f. E. **Fleischer**‖ precipitates the copper as subsulphocyanide (§ 119, 3, *b*), boils the washed precipitate with potash, and thus obtains suboxide of copper; or he precipitates with iodide of potassium and protochloride of tin, and thus obtains subiodide of copper. Either of these precipitates he brings in contact with sesquisulphate of iron, determines the protoxide of iron produced and calculates the copper therefrom.

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* Jahresber. von Kopp u. Will, 1860, 613.

† Zeitschr. f. anal. Chem. 9, 297.

‡ Annal. d. Chem. u. Pharm. 84, 84.

§ Chromate of potash is not suitable, as the chloride of copper impairs the distinctness of the end-reaction.

‖ Zeitschr. f. anal. Chem. 9, 255.

g. F. Fleitmann* precipitates the copper with zinc, brings the washed precipitate in contact with sesquichloride of iron and hydrochloric acid and determines the protochloride of iron produced. $Cu + Fe_2Cl_3 = CuCl + 2FeCl$.

h. H. Schwarz† adds xanthogenate of potash to the acetic acid solution of the copper, till no more precipitate is formed. The other heavy metals, except zinc, are precipitated from their acetic acid solution by this reagent, hence the copper must first be separated from them.

The methods *e* to *h* require previous precipitation or isolation of the copper, they cannot therefore deserve the preference before gravimetric methods except in very special cases.

§ 120.

6. TEROXIDE OF BISMUTH.

a. Solution.

Metallic bismuth, the teroxide, and all other compounds of that metal, are dissolved best in nitric acid, more or less diluted. It must be borne in mind that hydrochloric acid solutions of bismuth, if concentrated, cannot be evaporated without loss of chloride of bismuth.

b. Determination.

Bismuth is weighed in the form of *teroxide*, of *chromate*, of *sulphide* in the *metallic state*, or as *arseniate*. The compounds of bismuth are converted into teroxide by ignition, by precipitation as basic carbonate, or by repeated evaporation of the nitrate solution. These are sometimes preceded by separation as sulphide. The determination as metallic bismuth is frequently preceded by precipitation as sulphide or as basic chloride.

We may convert into

1. TEROXIDE OF BISMUTH:

a. By Precipitation as carbonate of bismuth. All compounds of bismuth which dissolve in nitric acid to nitrate. no other acid remaining in the solution.

b. By Ignition.

α. Salts of bismuth with readily volatile oxygen acids.

β. Salts of bismuth with organic acids.

c. By Evaporation. Bismuth in nitric acid solution.

d. By Precipitation as tersulphide of bismuth. All compounds of bismuth without exception.

2. CHROMATE OR ARSENIATE OF BISMUTH: All compounds named in 1, *a.*

3. SULPHIDE OF BISMUTH: The compounds of bismuth without exception.

4. METALLIC BISMUTH: The oxide and its salts, the sulphide, the basic chloride, in which latter form the bismuth may be precipitated out of all its solutions.

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* Annal. d. Chem. u. Pharm. 98, 141.

† Dingler's polyt. Journ. 190, 220 and 295; Zeitschr. f. anal. Chem. 8, 462.

1. *Determination of Bismuth as Teroxide.*

a. By Precipitation as Carbonate of Bismuth.

If the solution is concentrated add water, taking no notice of any precipitate of basic nitrate that may be formed. Mix with carbonate of ammonia in *very slight* excess, and heat for some time nearly to boiling; filter, dry the precipitate, and ignite in the manner directed § 116, 1 (Ignition of carbonate of lead); the process of ignition serves to convert the carbonate into the pure teroxide of bismuth. For the properties of the precipitate and residue, see § 86. The method gives accurate results, though generally a trifle too low, owing to the circumstance that carbonate of bismuth is not absolutely insoluble in carbonate of ammonia. Were you to attempt to precipitate bismuth, by means of carbonate of ammonia, from solutions containing sulphuric acid or hydrochloric acid, you would obtain incorrect results, since with the basic carbonate, basic sulphate or basic chloride would be precipitated, which are not decomposed by excess of carbonate of ammonia. Were you to filter off the precipitate without warming, a considerable loss would be sustained, as the whole of the basic carbonate would not have been separated (Expt. No. 74).

b. By Ignition.

α. Compounds like the carbonate or nitrate of bismuth are ignited in a porcelain crucible until their weight remains constant.

β. Compounds with organic acids are treated like the corresponding compounds of oxide of copper (§ 119, 1, *c.*).

c. By Evaporation.

The solution of the nitrate is evaporated, in a porcelain dish on the water-bath, till the neutral salt remains in syrupy solution;—add water, loosen the white crust that is formed with a glass rod from the sides, evaporate again on a water-bath, reprecipitate with water, and repeat the whole operation three or four times. After the dry mass on the water-bath has ceased to smell of nitric acid, it is allowed to cool thoroughly, and then treated with cold water containing a little nitrate of ammonia (1 in 500); after the residue and fluid have been a short time together, filter, wash with the weak solution of nitrate of ammonia, dry and ignite (§ 53). Results very satisfactory (J. Löwe*).

d. By Precipitation as Tersulphide of Bismuth.

Dilute the solution with water slightly acidulated with acetic acid (to prevent the precipitation of a basic salt), and precipitate with sulphuretted hydrogen water or gas; allow the precipitate to subside, and test a portion of the supernatant fluid with *sulphuretted hydrogen water*: if it remains clear, which is a sign that the bismuth is completely precipitated, filter (the filtrate should smell strongly of HS), and wash the precipitate with water containing sulphuretted hydrogen. Or mix with ammonia until the free acid is neutralized, then add sulphide of ammonium in excess, and allow to digest for some time.

The washed precipitate may now be weighed in three different forms, viz., as sulphide, as metal, or as oxide. The treatment in the two former cases will be described in 3 and 4: in the latter case proceed as follows:—

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* Journ. f. prakt. Chem. 74, 344.

Spread the filter out on a glass plate and remove the precipitate to a vessel by means of a jet of water from the wash-bottle—or, if this is not practicable, put the precipitate and filter together into the vessel—and heat gently with moderately strong nitric acid until complete decomposition is effected; the solution is then diluted with water slightly acidulated with acetic or nitric acid, and filtered, the filter being washed with the acidulated water; the filtrate is then finally precipitated as directed in *a*.

2. *Determination of Bismuth as Chromate* (J. LÖWE*).

Pour the solution of bismuth, which must be as neutral as possible, and must, if necessary, be first freed from the excess of nitric acid by evaporation on the water-bath, into a warm solution of pure bichromate of potassa in a porcelain dish, with stirring, and take care to leave the alkaline chromate slightly in excess. Rinse the vessel which contained the solution of bismuth with water containing nitric acid into the porcelain dish. The precipitate formed must be orange-yellow, and dense throughout; if it is flocculent, and has the color of the yolk of an egg, this is a sign that there is a deficiency of chromate of potassa; in which case add a fresh quantity of this salt, taking care, however, to guard against too great an excess, and boil until the precipitate presents the proper appearance. Boil the contents of the dish for ten minutes, with stirring; then wash the precipitate, first by repeated boiling with water and decantation on to a weighed filter, at last thoroughly on the latter with boiling water; dry at about 120°, and weigh. For the properties and composition of the precipitate, see § 86. Results very satisfactory.

3. *Determination of Bismuth as Sulphide.*

Precipitate the bismuth as sulphide according to 1, *d*. If the precipitate contains sulphur, extract the latter by boiling with solution of sulphite of soda, or by treatment with bisulphide of carbon (compare the determination of mercury as sulphide, § 118, 3), collect on a weighed filter, dry at 100°, and weigh.

The drying must be conducted with caution. At first the precipitate loses weight, by the evaporation of water, then it gains weight, from the absorption of oxygen. Hence you should weigh every half hour, and take the lowest weight as the correct one. Compare Expt. No. 52. Properties and composition, § 86, *g*.

The sulphide of bismuth cannot be conveniently converted into the metallic state by ignition in hydrogen, as its complete decomposition is a work of considerable time. As regards reduction with cyanide of potassium, see 4.

4. *Determination of Bismuth as Metal.*

The oxide, sulphide, or basic chloride that are to be reduced are fused in a porcelain crucible with five times their quantity of ordinary cyanide of potassium. The crucible must be large enough. In the case of oxide and basic chloride, the reduction is completed in a short time at a gentle heat; sulphide, on the other hand, requires longer fusion and a higher temperature. The operation has been successful, if on treatment with water metallic grains are obtained. These grains are first washed completely and rapidly with water, then with weak, and lastly with strong spirit, dried and weighed. If you have been reducing the sulphide, and on treating the fused mass with water a black powder (a mixture of bismuth with sulphide of bismuth) is visible, besides the metallic grains, it is necessary to fuse the former again with cyanide of potassium.

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* Journ. f. prakt. Chem. 67, 464.

It sometimes happens that the crucible is attacked, and particles of porcelain are found mixed with the metallic bismuth; to prevent this from spoiling the analysis, weigh the crucible together with a small dried filter before the experiment, collect the metal on the filter, dry and weigh the crucible with the filter and bismuth again. Results good (H. ROSE*).

The precipitation of bismuth as basic chloride, and the reduction of the latter with cyanide of potassium, has been recommended by H. ROSE.† The process is conducted as follows:—nearly neutralize any large excess of acid that may be present with potassa, soda, or ammonia, add chloride of ammonium in sufficient quantity (if hydrochloric acid is not already present), and then a rather large quantity of water. After allowing to stand some time, test whether a portion of the clear supernatant fluid is rendered turbid by a further addition of water; and then, if required, add water to the whole till the precipitation is complete. Finally filter, wash completely with cold water, dry and fuse according to the directions just given with cyanide of potassium. It is less advisable to dry the precipitate at 100°, weigh and calculate the metal present from the formula $2BiO_3 + BiCl_3$, as washing causes a slight alteration in its composition (unless a little hydrochloric acid is added to the wash-water, which is inconvenient when the precipitate is collected on a weighed filter) and if precipitated in the presence of sulphuric, phosphoric acids, &c., it is liable to contain small quantities of these acids. Results accurate.

5. *Determination of Bismuth as Arseniate.*

SCHEELE tells us that the arseniate of bismuth is quite insoluble in nitric acid, and this has been found correct. On this fact, SALKOWSKI‡ bases an estimation of bismuth. The solution of nitrate of bismuth must contain a little nitric acid, and be free from other acids. Precipitate with arsenic acid in moderate excess, stir without touching the sides of the beaker, allow to stand in the cold for a few hours, collect on a filter dried at 120°, and wash till the washings begin to show a slight turbidity. Dry at 120°, and weigh. The dried precipitate has the composition BiO_3,AsO_5,HO. It is not advisable to ignite the precipitate as the carbon of the filter exercises a reducing action even when nitrate of ammonia is used. The test-analyses communicated by SALKOWSKI gave 99·88 to 100·02 instead of 100.

§ 121.

7. OXIDE OF CADMIUM.

a. Solution.

Cadmium, its oxide, and all the other compounds insoluble in water, are dissolved in hydrochloric acid or in nitric acid.

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* Pogg. Annal. 91, 104, and 110, 136.

† *Ib.* 110, 425.

‡ Journ. f. prakt. Chem. 104, 170; Zeitschr. f. anal. Chem. 8, 205.

b. Determination.

Cadmium is weighed either in the form of *oxide*, or in that of *sulphide* (§ 87). It may also be weighed as *sulphate*, and in the absence of other bases precipitable by oxalic acid, it may be estimated volumetrically.

We may convert into

1. OXIDE OF CADMIUM:

a. By Precipitation. The compounds of cadmium which are soluble in water; the insoluble compounds, the acid of which is removed upon solution in hydrochloric acid; salts of cadmium with organic acids.

b. By Ignition. Salts of cadmium with readily volatile or easily decomposable inorganic oxygen acids.

2. SULPHIDE OF CADMIUM: All compounds of cadmium without exception.

3. SULPHATE OF CADMIUM: All compounds of cadmium, in the absence of other non-volatile substances.

1. *Determination as Oxide of Cadmium.*

a. By Precipitation.

Precipitate with carbonate of potassa, wash the precipitated carbonate of cadmium, and convert it, by ignition, into the state of pure oxide. The precipitation is conducted as in the case of zinc, § 108, 1, *a*. The oxide of cadmium which adheres to the filter may easily be reduced and volatilized; it is therefore necessary to be cautious. In the first place choose a thin filter, transfer the dried precipitate as completely as possible to the crucible, replace the filter in the funnel, and moisten it with nitrate of ammonia solution, allow to dry, and then burn carefully in a coil of platinum wire. Let the ash fall into the crucible containing the mass of the precipitate, ignite carefully, avoiding the action of reducing gases, and finally weigh. It is difficult to remove the last portions of carbonic acid, you must therefore repeat the ignition till the weight remains constant. Properties of precipitate and residue, § 87. Results generally a little too low.

b. By Ignition.

Same process as for zinc, § 108, 1, *c*.

2. *Determination as Sulphide of Cadmium.*

It is best to precipitate the moderately acid solution with sulphuretted hydrogen water or gas, which must be used in sufficient excess. The presence of a considerable quantity of free hydrochloric or nitric acid may—especially if the solution is not enough diluted—prevent complete precipitation, hence such an excess should be avoided, and the clear supernatant fluid should in all cases be tested, by the addition of a relatively large amount of sulphuretted hydrogen water to a portion, before being filtered. Alkaline solutions of cadmium may be precipitated with sulphide of ammonium. If the sulphide of cadmium is free from admixed sulphur, it may be at once collected on a weighed filter, washed first with diluted sulphuretted hydrogen water mixed with a little hydrochloric acid, then with pure water, dried at 100°, and weighed; if, on the contrary, it contains free sulphur, it may be purified by boiling with a solution of sulphite of soda, or by treatment with bisulphide of carbon (see Sulphide of Mercury, § 118, 3). Results accurate. The precipitation of sulphur may occasionally be obviated by adding to the cadmium solution cyanide of potassium till the precipitate first formed is redissolved, and then precipitating this solution with sulphuretted hydrogen.

If the sulphide of cadmium is not to be weighed as such, warm it, together with the filter, with moderately strong hydrochloric acid, till the precipitate has dissolved and the odor of sulphuretted hydrogen is no longer perceptible, filter and precipitate the solution as in 1, *a*, after having removed the excess of free acid for the most part by evaporation.

3. *Determination as Sulphate of Cadmium.*

Same process as for magnesia (§ 104, 1). The CdO,SO_3 may be rather strongly ignited without decomposition.

4. W. GIBBS* determines cadmium *volumetrically* by mixing the concentrated solution of the sulphate, nitrate, or chloride with excess of oxalic acid and a quantity of strong spirit, filtering, washing with alcohol, dissolving in hot hydrochloric acid and determining the oxalic acid with permanganate (§ 137). W. G. LEISON† obtained satisfactory results by this process.

Supplement to the Fifth Group.

§ 122.

8. PROTOXIDE OF PALLADIUM.

Protoxide of palladium is converted, for the purpose of estimation, into the *metallic state;* or—in many separations—into *double chloride of palladium and potassium.*

1. *Determination as Palladium.*

a. Neutralize the solution of protochloride of palladium almost completely with carbonate of soda, mix with solution of cyanide of mercury; and heat gently for some time, until the odor of prussic acid has gone off. A yellowish-white precipitate of protocyanide of palladium will subside; from dilute solutions, only after the lapse of some time. Wash first by decantation, then on the filter, dry thoroughly, ignite cautiously, finally over the gas blowpipe till the paracyanide of palladium first formed is decomposed, then ignite in hydrogen, since the palladium has been slightly oxidized. As soon as the lamp is removed stop the hydrogen to prevent absorption, and weigh the metal. If the solution contains nitrate of protoxide, evaporate it first with hydrochloric acid to dryness; as otherwise the precipitate obtained deflagrates upon ignition (WOLLASTON). Results exact.

b. Mix the solution of the protochloride or nitrate of protoxide of palladium with formiate of soda or potassa, and warm until no more carbonic acid escapes. The palladium precipitates in brilliant scales (DÖBEREINER).

c. Precipitate the acid solution of palladium with sulphuretted hydrogen, filter, wash with boiling water, roast, dissolve in hydrochloric acid and nitric acid, and precipitate as in *a.*

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* Zeitschr. f. anal. Chem. 7, 259.

† *Ib.* 10, 343.

Exposed to a moderate red heat *metallic palladium* becomes covered with a film varying from violet to blue, but at a higher temperature it recovers its lustre, which it keeps after being suddenly cooled, for instance, with cold water. This tarnishing and recovery of the metallic lustre is not attended with any perceptible difference of weight. Palladium which has taken up oxygen is immediately reduced in hydrogen, when cooled in the current of gas, it retains some absorbed hydrogen. Palladium requires the very highest degree of heat for its fusion. It dissolves readily in nitrohydrochloric acid, with difficulty in pure nitric acid, more easily in nitric acid containing nitrous acid, with difficulty in boiling concentrated sulphuric acid.

2. *Determination as Double Chloride of Palladium and Potassium.*

Evaporate the solution of chloride of palladium with chloride of potassium and nitric acid to dryness, and treat the mass when cold with alcohol of ·833 sp. gr., in which the double salt is insoluble. Collect on a weighed filter, dry at 100°, and weigh. Results a little too low, as traces of the double salt pass away with the alcohol washings (BERZELIUS). Instead of weighing the double salt you may ignite in hydrogen, remove the chloride of potassium with water and weigh the metal obtained. This method is indeed to be preferred, as it prevents any chloride of potassium in the precipitate from affecting the result.

The DOUBLE CHLORIDE OF PALLADIUM AND POTASSIUM consists of microscopic octahedra; it presents the appearance of a vermilion, or if the crystals are somewhat large, of a brown powder. It is very slightly soluble in cold water; it is almost insoluble in cold spirit of the above strength. It contains 26·806% palladium.

SIXTH GROUP.

TEROXIDE OF GOLD—BINOXIDE OF PLATINUM—TEROXIDE OF ANTIMONY—BINOXIDE OF TIN—PROTOXIDE OF TIN—ARSENIOUS AND ARSENIC ACIDS—(MOLYBDIC ACID).

§ 123.

1. TEROXIDE OF GOLD.

a. Solution.

Metallic gold, and all compounds of gold insoluble in water, are warmed with hydrochloric acid, and nitric acid is gradually added until complete solution is effected; or they are repeatedly digested with strong chlorine water. The latter method is resorted to more especially in cases where the quantity of gold to be dissolved is small, and mixed with foreign oxides, which it is wished to leave undissolved. According to W. SKEY* tincture of iodine, or for larger quantities of gold bromine water, is better than chlorine water. They give solutions freer from other bases than the chlorine water gives.

b. Determination.

Gold is always weighed in the *metallic state.* The compounds are brought into this form, either by ignition or by precipitation, as gold, or sulphide of gold.

We convert into

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* Zeitschr. f. anal. Chem. 10, 221.

METALLIC GOLD.

a. By Ignition. All compounds of gold which contain no fixed acid, or other body.

b. By Precipitation as metallic gold. All compounds of gold without exception in cases where *a* is inapplicable.

c. By Precipitation as tersulphide of gold. This method serves to effect the separation of gold from certain other metals which may be mixed with it in a solution.

Determination as Metallic Gold.

a. By Ignition.

Heat the compound, in a covered porcelain crucible, very gently at first, but finally to redness, and weigh the residuary pure gold. For properties of the residue, see § 88. The results are most accurate.

b. By Precipitation as Metallic Gold.

α. The solution is free from Nitric Acid. Mix the solution with a little hydrochloric acid, if it does not already contain some of that acid in the free state, and add a clear solution of sulphate of iron in excess; heat gently for a few hours until the precipitated fine gold powder has completely subsided; filter, wash, dry, and ignite according to § 52. A porcelain dish is a more appropriate vessel to effect the precipitation in than a beaker, as the heavy fine gold powder is more readily rinsed out of the former than out of the latter. There are no sources of error inherent in the method.

β. The solution of Gold contains Nitric Acid. Evaporate the solution, on a water-bath, to the consistence of syrup, adding from time to time hydrochloric acid; dissolve the residue in water containing hydrochloric acid, and treat the solution as directed in *α*. It will sometimes happen that the residue does not dissolve to a clear fluid, in consequence of a partial decomposition of the terchloride of gold into protochloride and metallic gold; however, this is a matter of perfect indifference.

γ. In cases where it is wished to avoid the presence of iron in the filtrate, the gold may be reduced by means of oxalic acid. To this end, the dilute solution—freed previously, if necessary, from nitric acid, in the manner directed in *β*—is mixed, in a beaker, with oxalic acid, or with oxalate of ammonia in excess, some sulphuric acid added (if that acid is not already present in the free state), and the vessel, covered with a glass plate, is kept standing for two days in a moderately warm place. At the end of that time, the whole of the gold will be found to have separated in small yellow scales, which are collected on a filter, washed first with dilute hydrochloric acid, then with water, dried, and ignited. If the gold solution contains a large excess of hydrochloric acid, the latter should be for the most part evaporated, before the solution is diluted and the oxalic acid added. If the gold solution contains chlorides of alkali metals, it is necessary to dilute largely, and allow to stand for a long time, in order to effect complete precipitation (H. ROSE).

δ. The gold may also be thrown down in the metallic form by hydrate of chloral* in the presence of potash. Warm the solution, add the chloral, then pure potash in excess and boil for a minute or so. The gold is precipitated with evolution of chloroform.

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* HAGER's pharmac. Centralhalle, 11, 393.

ε. Finally, gold may be thrown down by many metals, such as zinc, cadmium, magnesium, &c. The latter has been recommended by SCHEIBLER* for the analysis of the gold salts of organic bases. The precipitate is first washed with hydrochloric acid, then with water.

c. By Precipitation as Tersulphide of Gold.

Sulphuretted hydrogen gas is transmitted in excess through the dilute solution containing some free acid; the precipitate formed is speedily filtered off, without heating, washed, dried, and ignited in a porcelain crucible. For the properties of the precipitate, see § 88. No sources of error.

§ 124.

2. BINOXIDE OF PLATINUM.

a. Solution.

Metallic platinum, and the compounds of platinum which are insoluble in water, are dissolved by digestion, at a gentle heat, with nitrohydrochloric acid.

b. Determination.

Platinum is invariably weighed in the *metallic state*, to which condition its compounds are brought, either by precipitation as bichloride of platinum and chloride of ammonium, bichloride of platinum and chloride of potassium, or bisulphide of platinum, or by ignition, or by precipitation with reducing agents. All compounds of platinum, without exception, may, in most cases, be converted into platinum by either of these methods. Which is the most advantageous process to be pursued in special instances, depends entirely upon the circumstances. The reduction to the metallic state by simple ignition is preferable to the other methods, in all cases where admissible. The precipitation as bisulphide of platinum is resorted to exclusively to effect the separation of platinum from other metals.

Determination as Metallic Platinum.

a. By Precipitation as Bichloride of Platinum and Chloride of Ammonium.

The solution must be concentrated if necessary by evaporation on a water-bath. Mix, in a beaker, with ammonia until the excess of acid (that is, supposing an excess of acid to be present) is *nearly* saturated; add chloride of ammonium in excess, and mix the fluid with a pretty large quantity of absolute alcohol. Cover the beaker now with a glass plate, and let it stand for twenty-four hours, after which filter through a weighed asbestos filtering tube or an unweighed filter, wash the precipitate with spirit of wine of about 80 per cent., till the substances to be separated are removed, dry carefully, ignite according to § 99, 2, and weigh. In the case of large quantities the final ignition is advantageously conducted in a stream of hydrogen (§ 108, fig. 79), in order to be quite sure of effecting complete decomposition. For the properties of the precipitate and residue, see § 89. The results are satisfactory, though generally a little too low, as the bichloride of platinum and chloride of ammonium is not altogether insoluble in spirit of wine (Expt. No. 16); and as the fumes of chloride of ammonium are liable to carry away traces of the yet undecomposed double chloride, if the application of heat is not conducted with the greatest care.

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* Ber. der deutsch. chem. Gesellsch. 1869, 295.

If the precipitated bichloride of platinum and chloride of ammonium were weighed in that form, the results would be inaccurate, since, as I have convinced myself by direct experiments, it is impossible to completely free the double chloride, by washing with spirit of wine, from all traces of the chloride of ammonium thrown down with it, without dissolving at the same time, a notable portion of the double chloride. As a general rule, the results obtained by weighing the bichloride of platinum and chloride of ammonium in that form are one or two per cent. too high.

b. By Precipitation as Bichloride of Platinum and Chloride of Potassium.

Mix the solution, in a beaker, with potassa, until the greater part of the excess of acid (if there be any) is neutralized; add chloride of potassium slightly in excess, and finally a pretty large quantity of absolute alcohol; should your solution of platinum be very dilute, you must concentrate it previously to the addition of the alcohol. After twenty-four hours, collect the precipitate upon a weighed asbestos filtering tube, wash with spirit of wine of 80 per cent., dry thoroughly at 100°, and then convert into pure platinum according to § 97, 4, *a*, and weigh. For the properties of the precipitate and residue, see § 89.

The results are more accurate than those obtained by method *a*, since, on the one hand, the bichloride of platinum and chloride of potassium is more insoluble in spirit of wine than the corresponding ammonium salt; and, on the other hand, loss of substance is less likely to occur during ignition. To weigh the bichloride of platinum and chloride of potassium in that form would not be practicable, as it is impossible to remove, by washing with spirit of wine, all traces of the chloride of patassium thrown down with it, without, at the same time, dissolving a portion of the double chloride.

c. By Precipitation as Bisulphide of Platinum.

Precipitate the solution with sulphuretted hydrogen water or gas, according to circumstances, heat the mixture to incipient ebullition, filter, wash the precipitate, dry, and ignite according to § 52. For the properties of the precipitate and residue, see § 89. The results are accurate.

d. By Ignition.

Same process as for gold, § 123. For the properties of the residue, see § 89. The results are most accurate.

e. By Precipitation with Reducing Agents.

Various reducing agents may be employed to precipitate platinum from its solutions in the metallic state. The reduction is very promptly effected by sulphate of iron and potassa or soda (the protosesquioxide of iron being removed by subsequent addition of hydrochloric acid, HEMPEL), or by pure zinc or magnesium (the excess of which is removed by hydrochloric acid); somewhat more slowly, and only with application of heat, by alkaline formiates. Nitrate of suboxide of mercury also precipitates the whole of the platinum from solution of the bichloride; upon igniting the brown precipitate obtained, fumes of subchloride of mercury escape, and metallic platinum remains.

§ 125.

3. TEROXIDE OF ANTIMONY.

a. Solution.

Teroxide of antimony, and the compounds of that metal which are insoluble in water, or are decomposed by that agent, are dissolved in more or less concentrated hydrochloric acid. Metallic antimony is dissolved best in nitrohydrochloric acid. The ebullition of a hydrochloric acid solution of terchloride of antimony is attended with volatilization of traces of the latter; the concentration of a solution of the kind by evaporation involves accordingly loss of substance. Solutions so highly dilute as to necessitate a recourse to evaporation must therefore previously be supersaturated with potassa. Hydrochloric acid solutions of teroxide of antimony, which it is intended to dilute with water, must previously be mixed with tartaric acid, to prevent the separation of basic salt. In diluting an acid solution of antimonic acid in hydrochloric acid, the water must not be added gradually and in small quantities at a time, which would make the fluid turbid, but in sufficient quantity at once, which will leave the fluid clear.

b. Determination.

Antimony is weighed either as *tersulphide* or *antimoniate of teroxide* (SbO_4), in separations it is sometimes weighed as *metallic antimony*; or it is estimated volumetrically.

The oxides of antimony, and their salts with readily volatile or decomposable oxygen acids may be converted into antimoniate of teroxide by simple ignition. Antimony in solution is almost invariably first precipitated as sulphide, which is then, with the view of estimation, converted into anhydrous sulphide, or into antimoniate of teroxide, or determined volumetrically. Of the volumetric methods the first two are only to be used when the antimony is present as pure teroxide or terchloride.

1. *Precipitation as Sulphide of Antimony.*

Add to the antimony solution hydrochloric acid, if not already present, then tartaric acid, and dilute with water, if necessary. Introduce the clear fluid into a flask, closed with a doubly perforated cork; through one of the perforations passes a tube, bent outside at a right angle, which nearly extends to the bottom of the flask; through the other perforation passes another tube, bent outside twice at right angles, which reaches only a short way into the flask; the outer end of this tube dips slightly under water. Conduct through the first tube sulphuretted hydrogen gas, until it predominates strongly; put the flask in a moderately warm place, and after some time conduct carbonic acid into the fluid, until the excess of the other gas is almost completely removed. If there is no reason against it, from the presence of a large quantity of hydrochloric acid, or from the presence of nitric acid, it is well to heat the solution during the passing of the gas, finally even boiling. The precipitate is then denser, and may be very easily washed (SHARPLES*).

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* Zeitschr. f. anal. Chem. 10, 343.

If the amount of the precipitate is at all considerable, filter without intermission through a weighed filter, wash rapidly and thoroughly with water mixed with a few drops of sulphuretted hydrogen water, dry at 100°, and weigh. The precipitate so weighed always retains some water, and may, besides, contain free sulphur; in fact, it always contains the latter in cases where the antimony solution, besides teroxide or terchloride, contains antimonic acid or pentachloride of antimony, since the precipitation under these circumstances is preceded by a reduction of the higher oxide or chloride to teroxide or terchloride, accompanied by separation of sulphur (H. Rose). A further examination of the precipitate is accordingly indispensable. To this end, treat a sample of the weighed precipitate with strong hydrochloric acid. If

a. The sample dissolves to a clear fluid, this is a proof that the precipitate only contains SbS_3; but if

b. Sulphur separates, this shows that free sulphur is present.

In *case a* (in order to remove the water retained at 100°) the greater portion of the dried precipitate is weighed in a porcelain boat, which is then inserted into a glass tube, about 2 decimetres long; a slow current of dry carbonic acid is transmitted through the latter, and the boat cautiously heated by means of a lamp, moved to and fro under it, until the orange precipitate becomes black. The precipitate is then allowed to cool in the current of carbonic acid, and weighed; from the amount found, the total quantity of anhydrous sulphide of antimony contained in the entire precipitate is ascertained by a simple calculation. The results are accurate. Expt. No. 75 gave 99·24 instead of 100. But if the precipitate is simply dried at 100°, the results are about 2 per cent. too high—see the same experiment. For the properties of the precipitate, see § 90.

In *case b*, the precipitate is subjected to the same treatment as in *a*, with this difference only, that the contents of the boat are heated much more intensely, and the process is continued until no more sulphur is expelled. This removes the whole of the admixed sulphur; the residue consists of pure tersulphide of antimony. It must be completely soluble in fuming hydrochloric acid on heating.

If the amount of the precipitate is small, collect it in a weighed asbestos filtering tube, dry in a slow current of carbonic acid at a gentle heat, heat finally rather more strongly till the sulphide has turned black and any free sulphur present has volatilized, allow to cool, replace the gas in the tube by air and weigh. Results quite satisfactory.*

According to Bunsen it is best to convert the sulphide of antimony into antimoniate of teroxide (see 2).

For the method of estimating the antimony in the sulphide volumetrically and indirectly, see 3, *c*.

2. *Determination as Antimoniate of Teroxide.*

a. In the case of teroxide of antimony or a compound of the same with an easily volatile or decomposable oxygen acid, evaporate carefully with nitric acid, and ignite finally for some time till the weight is constant. The experiment may be safely made in a platinum crucible. With antimonic acid, the evaporation with nitric acid is unnecessary.

b. If sulphide of antimony is to be converted into antimoniate of teroxide, one of the two following methods given by **Bunsen**[*] is employed:—

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* Zeitschr. f. anal. Chem. 8, 155.

a. Moisten the dry sulphide of antimony with a few drops of nitric acid of 1·42 sp. gr., then treat, in a weighed porcelain crucible, with concave lid, with 8—10 times the quantity of fuming nitric acid,[†] and let the acid gradually evaporate on the water-bath. The sulphur separates at first as a fine powder, which, however, is readily and completely oxidized during the process of evaporation. The white residual mass in the crucible consists of antimonic acid and sulphuric acid, and may by ignition be converted, without loss, into antimoniate of teroxide of antimony. If the sulphide of antimony contains a large excess of free sulphur, this must first be removed by washing with bisulphide of carbon.

β. Mix the sulphide of antimony with 30—50 times its quantity of pure oxide of mercury,[‡] and heat the mixture gradually in an open porcelain crucible. As soon as oxidation begins, which may be known by the sudden evolution of gray mercurial fumes, moderate the heat. When the evolution of mercurial fumes diminishes raise the temperature again, always taking care, however, that no reducing gases come in contact with the contents of the crucible. Remove the last traces of oxide of mercury over the blast gas-lamp, then weigh the residual fine white powder of antimoniate of teroxide of antimony. As oxide of mercury generally leaves a trifling fixed residue upon ignition; the amount of this should be determined once for all, the oxide of mercury added approximately weighed, and the corresponding amount of fixed residue deducted from the antimoniate of teroxide of antimony. The volatilization of the oxide of mercury proceeds much more rapidly when effected in a platinum crucible, instead of a porcelain one. But, if a platinum crucible is employed, it must be effectively protected from the action of antimony upon it, by a *good lining* of oxide of mercury.[§] If the sulphide of antimony contains free sulphur, this must first be removed by washing with bisulphide of carbon, before the oxidation can be proceeded with, since otherwise a slight deflagration is unavoidable.

3. *Volumetric Methods.*

a. Oxidation of Teroxide of Antimony to Antimonic Acid by Iodine (**Mohr**[‖]).

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[*] Annal d. Chem. u. Pharm. 106, 3.

[†] Nitric acid of 1·42 sp. gr. is not suitable for this purpose, as its boiling point is almost 10° above the fusing point of sulphur, whereas fuming nitric acid boils at 86°, consequently below the fusing point of sulphur. With nitric acid of 1·42 sp. gr., therefore, the separated sulphur fuses and forms drops, which obstinately resist oxidation.

[‡] It is best to use that prepared in the wet way (§ 60, 4)

[§] This is effected best, according to **Bunsen**, in the following way: Soften the sealed end of a common test-tube before the glass-blower's lamp; place the softened end in the centre of the platinum crucible, and blow into it, which will cause it to expand and assume the exact form of the interior of the crucible. Crack off the bottom of the little flask so formed, and smooth the sharp edge cautiously by fusion. A glass is thus obtained, open at both ends, which exactly fits the crucible. To effect the lining by means of this instrument, fill the crucible loosely with oxide of mercury up to the brim, then force the glass gradually and slowly down to the bottom of the crucible, occasionally shaking out the oxide of mercury from the interior of the glass. The inside of the crucible is thus covered with a layer of oxide of mercury ½—1 line thick, which, after the removal of the glass, adheres with sufficient firmness, even upon ignition.

[‖] His Lehrbuch der Titrirmethode, 3 Aufl. 276.

The oxidation is effected in alkaline solution, and proceeds according to the equation: $SbO_3 + I_2 + 2NaO = SbO_5 + 2NaI$. This method cannot be relied on except under very definite conditions; for teroxide of antimony has not invariably the same tendency, in alkaline solution, to change to antimonic acid; but this tendency is greater in presence of a large proportion of alkaline carbonate, than in presence of a small proportion, and becomes constant only in presence of a certain excess of alkaline carbonate. To obtain accurate results, therefore, it is necessary to proceed as follows:—

Dissolve a portion of the compound, containing about ·1 grm. teroxide of antimony, in about 10 c.c. of tartaric acid and water, and add solution of carbonate of soda till the fluid is about neutral. Add now 20 c.c. of a cold saturated solution of bicarbonate of soda; the fluid will remain clear; add some starch paste, and finally, drop by drop, standard solution of iodine (§ 146), until the fluid, after being stirred, remains just blue. The disappearance of the color, a short time after, must not induce the operator to add any more solution of iodine; 2 eq. of the iodine used correspond to 1 eq. teroxide of antimony.

The results obtained are quite satisfactory (Expt. No. 76). I cannot recommend the use of the monocarbonate of soda which Mohr employed in his experiments, as that salt has of itself the property of fixing a considerable proportion of iodine, which varies, moreover, with the quantity of water used (Expt. No. 77); whilst this is not the case with the bicarbonate (Expt. No. 78). Comp. also § 127, 5, *a*, 1, and Expt. No. 79.

b. Oxidation of Teroxide of Antimony in hydrochloric acid solution by chromate or permanganate of potash.

F. Kessler's* first description of this method was so wanting in precision, that it could not be depended upon. However, he has since† determined most accurately the conditions under which teroxide of antimony in acid solution may be satisfactorily titrated either with chromate of potash (the excess of the standard solution being determined with sulphate of iron) or with permanganate of potash.

I. *Titration with Bichromate of Potash.*

1. Requisites.

a. Standard Solution of Arsenious Acid. Dissolve exactly 5 grm. pure arsenious acid by the aid of some soda solution, add hydrochloric acid till slightly acid, then 100 c.c. more of hydrochloric acid of 1·12 sp. gr., and dilute to 1000 c.c. Each c.c. contains ·005 grm. arsenious acid and corresponds to ·007374 teroxide of antimony.

β. Solution of Bichromate of Potassa. Dissolve about 2·5 grm. to 1 litre.

γ. Solution of Protosulphate of Iron. Dissolve about 1·1 grm. iron wire in 20 c.c. dilute sulphuric acid (1 to 4), filter, and dilute to 1 litre.

δ. Solution of Ferricyanide of Potassium. Should be tolerably dilute and freshly prepared.

2. Determination of the Solutions.

a. Relation between the Solution of Chromate and the Solution of Iron. Run into a beaker 10 c.c. of the chromate solution from the burette, add 5 c.c. of hydrochloric acid and 50 c.c. water, and then add iron solution from a burette till the fluid is green. Continue adding the iron solution, a c.c. at a time, testing after each addition whether a drop of the fluid, when brought in contact with a drop of the ferricyanide of potassium, on a porcelain plate, manifests a distinct protoxide of iron reaction. As soon as this point is attained, add ·5 c.c. of chromate solution and then iron solution two drops at a time, till the blue reaction just occurs. Now read off both burettes, and calculate how much chromate solution corresponds to 10 c.c. of iron solution. This experiment is to be repeated before every fresh series of analyses, as the iron solution gradually oxidizes.

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* Pogg. Annal. 95, 204.

† *Ib.* 118, 17; and Zeitschr. f. anal. Chem. 2, 383.

β. *Relation between the Chromate Solution and the Solution of Arsenious Acid.* Transfer 10 c.c. of the arsenic solution to a beaker, add 20 c.c. hydrochloric acid of 1·2 sp. gr., and 80—100 c.c.* water, run in chromate solution till the yellow color of the fluid shows an excess, wait a few minutes, add excess of iron solution, then again ·5 chromate solution, and finally again iron solution till the end-reaction appears (see above). Deduct from the total quantity of chromate solution employed, the amount corresponding to the iron used, and from the datum thus afforded calculate how much teroxide of antimony corresponds to 100 c.c. of chromate solution; in other words, how much SbO_3 is converted by the quantity of chromate mentioned into SbO_5.

3. THE ACTUAL ANALYSIS.

In the absence of organic matter, heavy metallic oxides, and other bodies which are detrimental to the reaction, dissolve the substance containing teroxide of antimony, at once in hydrochloric acid. The solution should contain not less than $\frac{1}{6}$ of its volume of hydrochloric acid of 1·12 sp. gr. It is not advisable, on the other hand, that it should contain more than $\frac{1}{2}$, otherwise the end-reaction with ferricyanide of potassium is slower in making its appearance and loses its nicety. Tartaric acid cannot be employed as a solvent, since it interferes with the action of chromic acid on protoxide of iron. Now proceed as directed in 2. If the direct determination of the hydrochloric acid solution is not practicable, precipitate it with sulphuretted hydrogen. Wash the precipitate, transfer it, together with the filter, to a small flask; treat it with a sufficiency of hydrochloric acid, dissolve by digestion on the water-bath, add a sufficient quantity of a nearly saturated solution of chloride of mercury in hydrochloric acid of 1·12 sp. gr. to remove the sulphuretted hydrogen, and then proceed as directed.

II. *Titration with Permanganate of Potash.*

Here also the fluid must contain at least $\frac{1}{6}$ of its volume of hydrochloric acid of 1·12 sp. gr. The permanganate solution, which may contain about 1·5 grm. of the crystallized salt in a litre, is added to permanent reddening. The end-reaction is exact, and the oxidation of the teroxide of antimony to antimonic acid goes on uniformly, although the degree of dilution may vary, provided the above relation between hydrochloric acid and water is kept up. It is not well that the hydrochloric acid should exceed $\frac{1}{3}$ of the volume of the fluid, as in that case the end-reaction would be too transitory. Tartaric acid, at least in the proportion to teroxide of antimony in which it exists it tartar emetic, does not interfere with the reaction. Hence the permanganate may be standardized by the aid of solution of tartar emetic of known strength.

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* The water must be measured, for the action of chromic acid on arsenious acid (and also on teroxide of antimony) is normal only if the fluid contains at least one-sixth of its volume of hydrochloric acid of 1·12 sp. gr.

If you have to analyse sulphide of antimony, proceed as directed I, 3; make the fluid mixed with chloride of mercury up to a certain volume, allow to settle, and use a measured portion of the *perfectly clear* solution for the experiment.

My own experiments* have shown that **Kessler**'s methods are also suitable for the estimation of very small quantities of antimony.

c. Volumetric Estimation by determining the Sulphuretted Hydrogen given up by the Sulphide (R. **Schneider**†).

Both tersulphide and pentasulphide yield under the action of boiling hydrochloric acid 3 eq. of sulphuretted hydrogen for every 1 eq. of antimony. Hence, if the amount of the gas evolved under such circumstances is estimated, the amount of antimony is known.

For decomposing the sulphide and absorbing the gas the same apparatus serves as **Bunsen** employs for his iodimetric analyses (§ 130). The size of the boiling flask should depend on the quantity of sulphide; for quantities up to ·4 grm. SbS_3, a flask of 100 c.c. is large enough; for ·4—1 grm., use a 200 c.c. flask. The body of the flask should be spherical, the neck rather narrow, long, and cylindrical. If the sulphide of antimony is on a filter, put both together into the flask. The hydrochloric acid should not be too concentrated.

The determination of the sulphuretted hydrogen is best conducted according to the method given in § 148, *b*. The results obtained by **Schneider** are satisfactory. If the precipitate contains chloride of antimony, the results are of course false, and this would actually be the case if on precipitation with sulphuretted hydrogen the addition of the tartaric acid were omitted.

§ 126.

4. Protoxide of Tin, and 5. Binoxide of Tin.

a. Solution.

In dissolving compounds of tin soluble in water, a little hydrochloric acid is added to insure a clear solution. Nearly all the compounds of tin insoluble in water dissolve in hydrochloric acid or in aqua regia. The hydrate of metastannic acid may be dissolved by boiling with hydrochloric acid, decanting the fluid, and treating the residue with a large proportion of water. Ignited binoxide of tin, and compounds of the binoxide insoluble in acids, are prepared for solution in hydrochloric acid, by reducing them to the state of a fine powder, and fusing in a silver crucible with hydrate of potassa, or soda, in excess. Metallic tin is dissolved best in aqua regia; the solution frequently contains metastannic chloride mixed with the bichloride of tin (**Th. Scheerer**‡). It is generally determined, however, by converting it into binoxide, without previous solution. Acid solutions of binoxide of tin, which contain hydrochloric acid, or a chloride, cannot be concentrated by evaporation, not even after addition of nitric acid or sulphuric acid, without volatilization of bichloride of tin taking place.

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* Zeitschr. f. anal. Chem. 8, 155.

† Pogg. Annal. 110, 634.

‡ Journ. f. prakt. Chem. N. F. 3, 472.

b. Determination.

Tin is weighed in the form of *binoxide*, into which it is converted, either by the agency of nitric acid, or by precipitation as hydrated binoxide, or by precipitation as sulphide. A great many volumetric methods of estimating tin have been proposed. They all depend on obtaining the tin in solution in the condition of protochloride, and converting this into bichloride either in alkaline or acid solution. A few only yield satisfactory results.

We may convert into

BINOXIDE OF TIN :

a. By the agency of nitric acid. Metallic tin, and those compounds of tin which contain no fixed acid, provided no compounds of chlorine be present.

b. By Precipitation as hydrated binoxide. All compounds of tin containing volatile acids, provided no non-volatile organic substances nor sesquioxide of iron be present.

c. By Precipitation as sulphide. All compounds of tin without exception.

In methods *a* and *c*, it is quite indifferent whether the tin is present in the state of protoxide or in that of binoxide. The method *b* requires the tin to be present in the state of binoxide. The volumetric methods may be employed in all cases; but the estimation is simple and direct only where the tin is in solution as protochloride and free from other oxidizable bodies, or can readily be brought into this state. For the methods of determining the protoxide and binoxide in presence of each other, I refer to Section V.

1. *Determination of Tin as Binoxide.*

a. By Treating with nitric acid.

This method is resorted to principally to convert the metallic tin into binoxide. For this purpose the finely-divided metal is put into a capacious flask, and moderately concentrated pure nitric acid (about 1·3 sp. gr.) gradually poured over it; the flask is covered with a watch glass. When the first tumultuous action of the acid has somewhat abated, a gentle heat is applied until the metastannic hydrate formed appears of a pure white color, and further action of the acid is no longer perceptible. The contents of the flask are then transferred to a porcelain dish and evaporated on a water-bath nearly to dryness, water is then added, and the precipitate is collected on a filter, washed, till the washings scarcely redden litmus paper, dried, ignited, and weighed. The ignition is effected best in a small porcelain crucible, according to § 53; still a platinum crucible may also be used. A simple red heat is not sufficient to drive off all the water; the ignition must therefore be finished over a gas blowpipe. Compounds of tin which contain no fixed substances may be converted into binoxide by treating them in a porcelain crucible with nitric acid, evaporating to dryness, and igniting the residue. If sulphuric acid be present, the expulsion of that acid may be promoted, in the last stages of the process, by carbonate of ammonia, as in the case of bisulphate of potassa (§ 97); here also the heat must be increased as much as possible at the end. For the properties of the residue, see § 91. There are no inherent sources of error.

b. By Precipitation as hydrate of binoxide.

The application of this method presupposes the whole of the tin to be present in the state of binoxide or bichloride. Therefore, if a solution contains protoxide, either mix with chlorine water, or conduct chlorine gas into it, or heat gently with chlorate of potassa, until the conversion of the protoxide into binoxide is effected. When this has been done, add ammonia until a permanent precipitate just begins to form, and then hydrochloric acid, drop by drop, until this precipitate is completely redissolved; by this means a large excess of hydrochloric acid in the solution will be avoided. Add to the fluid so prepared a concentrated solution of nitrate of ammonia (or sulphate of soda), and apply heat for some time, whereupon the whole of the tin will precipitate as hydrate of binoxide. Decant three times on to a filter, then collect the precipitate on the latter, wash thoroughly, dry, and ignite. To make quite sure that the whole of the tin has separated, you need simply, before proceeding to filter, add a few drops of the clear supernatant fluid to a hot solution of nitrate of ammonia, or sulphate of soda, when the formation or non-formation of a precipitate will at once decide the question. The tin is also precipitated from metastannic chloride by the above reagents.

This method, which we owe to J. Löwenthal, has been repeatedly tested by him in my own laboratory,* is easy and convenient, and gives very accurate results. The decomposition is expressed by the equation, $SnCl_2 + 2(NH_4O,NO_5) + 2HO = SnO_2 + 2NH_4Cl + 2(NO_5,HO)$, or in precipitating with sulphate of soda: $SnCl_2 + 4(NaO,SO_3) + 2HO = SnO_2 + 2NaCl + 2(NaO,HO,2SO_3)$.

Tin may also, according to H. Rose,† be completely precipitated from solutions of the binoxide or bichloride, by sulphuric acid. If the solution contains metastannic acid or metachloride of tin, the precipitation is effected without extraordinary dilution; on the other hand, if it contains the other modifications of the binoxide or bichloride, very considerable dilution is necessary. If free hydrochloric acid is absent, the precipitation is rapid; in other cases 12 or 24 hours at least are required for perfect precipitation. Allow to settle thoroughly, before filtering, wash well (if hydrochloric acid was present, till the washings give no turbidity with nitrate of silver), dry and ignite, at last intensely with addition of some carbonate of ammonia. The results obtained by Oesten, and communicated by H. Rose, are exact.

c. By Precipitation as Protosulphide or Bisulphide of Tin.

Precipitate the dilute moderately acid solution with sulphuretted hydrogen water or gas. If the tin was present in the solution in the form of protoxide, and the precipitate consists accordingly of the brown protosulphide, keep the solution, supersaturated with sulphuretted hydrogen, standing for half an hour in a moderately warm place, and then filter. If, on the other hand, the solution contain a salt of binoxide of tin or metastannic oxide, and the precipitate is yellow and consists of bisulphide mixed with binoxide, or yellowish brown and consists of hydrated metastannic sulphide mixed with metastannic acid (Barfoed, p. 155, Th. Scheerer‡), put the fluid, loosely covered, in a warm place, until the odor of sulphuretted hydrogen has nearly gone off, and then filter. The washing of the bisulphide of tin precipitate which has a great inclination to pass through the filter, is best effected with a concentrated solution of chloride of sodium, the remains of the latter being got rid of by a solution of acetate of ammonia containing a small excess of acetic acid. If there is no objection to having the latter salt in the filtrate, the washing may be entirely effected by its means (BUNSEN*). Transfer the dry precipitate as completely as possible to a watch glass, burn the filter carefully in a weighed porcelain crucible, moisten the ash with nitric acid, ignite, allow to cool, add the precipitate, cover the crucible, heat gently for some time (slight decrepitation often occurs), remove the lid and heat gently with access of air, till sulphurous acid has almost ceased to be formed. (If too much heat is applied at first, bisulphide of tin volatilizes, the fumes of which give binoxide.) Now heat strongly, allow to cool, and heat repeatedly with pieces of carbonate of ammonia to a high degree, to drive out the last portions of sulphuric acid. When the weight remains constant the experiment is ended (H. ROSE). For the properties of the precipitates, see § 91. The results are accurate.

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* Journ. f. prakt. Chem. 56, 366.

† Pogg. Annal. 112, 164.

‡ Journ. f. prakt. Chem. N. F. 3, 472.

2. *Volumetric Methods.*

The determination of tin by the conversion of the proto- into bichloride with the aid of oxidizing agents (bichromate of potassa, iodine, permanganate of potassa, &c.) offers peculiar difficulties, inasmuch as on the one hand the protochloride of tin takes up oxygen from the air and from the water used for dilution, with more or less rapidity, according to circumstances; and on the other hand, the energy of the oxidizing agent is not always the same, being influenced by the state of dilution and the presence of a larger or smaller excess of acid.

In the following methods, these sources of error are avoided or limited in such a manner as to render the results satisfactory.

1. *Estimation of Protochloride of Tin by Iodine in Alkaline Solution (after* LENSSEN†).

Dissolve the protosalt of tin or the metallic tin‡ in hydrochloric acid (preferably in a stream of carbonic acid), add Rochelle salt, then bicarbonate of soda in excess. To the clear slightly alkaline solution thus formed add some starch-solution, and afterwards the iodine solution of § 146, till a permanent blue coloration appears. 1 eq. free iodine used corresponds to 1 eq. tin.

LENSSEN'S results are entirely satisfactory.

2. *Estimation of Protochloride of Tin, after addition of Sesquichloride of Iron.*

The fact that protochloride of tin in acid solution can be far more accurately oxidized by oxidizing agents after being mixed with sesquichloride of iron (or even with chloride of copper) than without this addition, was first settled by LÖWENTHAL.§ Subsequently STROMEYER‖

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* Annal. d. Chem. u. Pharm. 106, 13.

† Journ. f. prakt. Chem. 78, 200; Annal. d. Chem. u. Pharm. 114, 113.

‡ The solution of metallic tin is much assisted by the presence of platinum foil, which is accordingly added. LENSSEN found this addition of platinum to be objectionable; but no other experimenter has observed that it interferes with the accuracy of the results.

§ Journ. f. prakt. Chem. 76, 484.

‖ Annal. d. Chem. u. Pharm. 117, 261.

published some experiments leading to the same results, together with practical remarks on the best way of carrying out the method in different cases. The processes thus originated, and which have been well tested, are as follows :—

a. The given substance is a proto-salt of tin. Dissolve in pure sesquichloride of iron (free from protochloride) with addition of hydrochloric acid, dilute and add standard permanganate from the burette. Now make another experiment with the same quantity of water similarly colored with sesquichloride of iron to ascertain how much permanganate is required to tinge the liquid, and subtract the quantity so used from the amount employed in the actual analysis, and from the remainder calculate the tin.

The reaction between the tin salt and the iron solution is $SnCl + Fe_2Cl_3 = SnCl_2 + 2FeCl$. The solution thus contains protochloride of iron in the place of proto-salt of tin, the former being, as is well known, far less susceptible of alteration from the action of free oxygen than the latter. 2 eq. iron found corresponds to 1 eq. tin. It must not be forgotten that the titration takes place in presence of hydrochloric acid, see p. 219, γ. The results cannot be considered accurate unless the standardizing of the permanganate and the analysis take place under similar conditions as regards dilution and amount of hydrochloric acid.

b. The given substance is metallic tin. Either dissolve in hydrochloric acid—preferably with addition of platinum and in an atmosphere of carbonic acid—and treat the solution according to *a*, or place the substance at once in a concentrated solution of sesquichloride of iron, mixed with a little hydrochloric acid ; under these circumstances it will, if finely divided, dissolve quickly even in the cold and without evolution of hydrogen. Gentle warming is unobjectionable. Now add the permanganate. The reaction is $Sn + 2Fe_2Cl_3 = SnCl_2 + 4FeCl$, therefore every 4 eq. iron found reduced correspond to 1 eq. tin. The results are of course only correct when iron is not present. Where this is the case, proceed with the impure tin solution according to *c*.

c. The given substance is bichloride of tin, or binoxide of tin, or a compound of tin containing iron. Dissolve in water with addition of hydrochloric acid, place a plate of zinc in the solution and allow to stand twelve hours, then remove the precipitated tin with a paint-brush, wash it, dissolve in sesquichloride of iron, and proceed as in *b*.

d. The given substance is pure bisulphide of tin, precipitated out of an acid solution of binoxide free from protoxide. Mix with sesquichloride of iron, heat gently, filter off the sulphur, and then add the permanganate. 4 eq. iron correspond to 1 eq. tin, for $SnS_2 + 2Fe_2Cl_3 = SnCl_2 + 4FeCl + 2S$. The results obtained by STROMEYER are quite satisfactory. As regards the precipitated sulphide of tin, see BARFOED, p. 155.

§ 127.

6. ARSENIOUS ACID, and 7. ARSENIC ACID.

a. Solution.

The compounds of arsenious and arsenic acids which are not soluble in water are dissolved in hydrochloric acid or in nitrohydrochloric acid. Some native arseniates require fusing with carbonate of soda.

Metallic arsenic, sulphide of arsenic, and metallic arsenides are dissolved in fuming nitric acid or nitrohydrochloric acid, or a solution of bromine in hydrochloric acid; those metallic arsenides which are insoluble in these menstrua are fused with carbonate of soda and nitrate of potassa, by which means they are converted into soluble arseniates of the alkalies and insoluble metallic oxides, or they may be suspended in potassa solution and treated with chlorine (§ 164, B, 7). In this last manner too, sulphide of arsenic, dissolved in concentrated potassa, may be very easily rendered soluble. All solutions of compounds of arsenic which have been effected by long heating with fuming nitric acid, or by warming with excess of nitrohydrochloric acid, or chlorine, contain arsenic acid. A solution of arsenious acid in hydrochloric acid cannot be concentrated by evaporation, since chloride of arsenic would escape with the hydrochloric acid fumes. This, however, less readily takes place if the solution contains arsenic acid; in fact, it only occurs in the presence of a large proportion of hydrochloric acid (for instance, half the volume of hydrochloric acid of 1·12 sp. gr.*). It is therefore advisable in most cases where a hydrochloric acid solution containing arsenic is to be concentrated, previously to render the same alkaline.

b. Determination.

Arsenic is weighed as *arseniate of lead*, as *arseniate of magnesia and ammonia*, as *arseniate of magnesia*, as *arseniate of uranium*, or as *tersulphide of arsenic*. The determination as arseniate of magnesia and ammonia is sometimes preceded by precipitation as arsenio-molybdate of ammonia. The method recommended by BERTHIER and modified by v. KOBELL of separating the arsenic as basic arseniate of iron is only used in separations. Arsenic may be estimated also in an *indirect way*, and by *volumetric methods*.

We may convert into

1. ARSENIATE OF LEAD: Arsenious and arsenic acids in aqueous or nitric acid solution. (Acids or halogens forming fixed salts with lead, and also ammonia salts, must not be present.)

2. ARSENIATE OF MAGNESIA AND AMMONIA, or ARSENIATE OF MAGNESIA:

a. By direct Precipitation. Arsenic acid in all solutions free from bases or acids precipitable by magnesia or ammonia.

b. Preceded by Precipitation as arsenio-molybdate of ammonia. Arsenic acid in all cases where no phosphoric acid is present, little or no hydrochloric acid, nor any substance which decomposes molybdic acid.

3. ARSENIATE OF URANIUM: Arsenic acid in all combinations soluble in water and acetic acid.

4. TERSULPHIDE OF ARSENIC: All compounds of arsenic without exception.

Arsenic may be determined volumetrically in a simple and exact manner, whether present in the form of arsenious acid or an alkaline arsenite, or as arsenic acid or an alkaline arseniate. The volumetric methods have now almost entirely superseded the indirect gravimetric methods formerly employed to effect the estimation of arsenious acid.

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* Zeitschr. f. anal. Chem. 1, 448.

1. *Determination as Arseniate of Lead.*

a. Arsenic Acid in Aqueous Solution.

A weighed portion of the solution is put into a platinum or porcelain dish, and a weighed amount of recently ignited pure oxide of lead added (about five or six times the supposed quantity of arsenic acid present); the mixture is cautiously evaporated to dryness, and the residue heated to gentle redness, and maintained some time at this temperature. The residue is arseniate of lead + oxide of lead. The quantity of arsenic acid is now readily found by subtracting from the weight of the residue that of the oxide of lead added. For the properties of arseniate of lead, see § 92. The results are accurate, provided the residue be not heated beyond gentle redness.

b. Arsenious Acid in Solution.

Mix the solution with nitric acid, evaporate to a small bulk, add a weighed quantity of oxide of lead in excess, evaporate to dryness, and ignite the residue most cautiously in a covered crucible, until the whole of the nitrate of lead is decomposed. The residue consists here also of arsenic acid + oxide of lead. This method requires considerable care to guard against loss by decrepitation upon ignition of the nitrate of lead.

2. *Estimation as Arseniate of Magnesia and Ammonia, or Arseniate of Magnesia.*

a. By Direct Precipitation.

This method, which was first recommended by LEVOL, presupposes the whole of the arsenic in the form of arsenic acid. Where this is not the case, the solution is gently heated, in a capacious flask, with hydrochloric acid, and chlorate of potassa added in small portions, until the fluid emits a strong smell of chlorous acid; it is then allowed to stand at a gentle heat until the odor of this gas is nearly gone off.

The arsenic acid solution is now mixed with ammonia in excess, which must not produce turbidity, even after standing some time; magnesia mixture is then added (§ 62, 6). The fluid, which smells strongly of ammonia, is allowed to stand 24 or 48 hours in the cold well covered and then filtered through a weighed filter. The precipitate is then transferred to the filter, with the aid of portions of the filtrate so as to use no more washing water than necessary, and washed with small quantities of a mixture of three parts water and one part ammonia, till the washings on being mixed with nitric acid and nitrate of silver show no opalescence. The precipitate is dried at 102° to 103°, and weighed. It has the formula $2MgO,NH_4O,AsO_5 + aq.$[*] As the drying of arseniate of ammonia and magnesia till its weight is constant requires much time and repeated weighings, it is a great advantage that we can now convert it without loss of arsenic into arseniate of magnesia ($2MgO,AsO_5$), thanks to the researches of H. ROSE,[†] WITTSTEIN[‡] and PULLER.[§] For this purpose first transfer the dried precipitate as completely as possible to a watch-glass, saturate the filter with a solution of nitrate of ammonia, dry and burn it cautiously in a porcelain crucible. After cooling, transfer the precipitate to the crucible, heat in an air-bath to about 130°, continue heating for 2 hours on a sand-bath, then heat for an hour or two on an iron plate a little more strongly, and when the ammonia has been thus entirely expelled ignite strongly for some time over the lamp. The process may be shortened by conducting the heating in a ROSE's crucible in a slow current of oxygen. The ammonia may then be driven off in 10 minutes, and after the precipitate has been at last strongly heated it will be ready to weigh. For the properties of the arseniate of ammonia and magnesia and the arseniate of magnesia, see § 92. The method yields satisfactory results, since the small loss of precipitate dissolved in the filtrate and washings is counterbalanced by the presence of a trace of basic sulphate of magnesia (PULLER). PULLER with a quantity of ·37 grm. arseniate of magnesia and ammonia lost only a fraction of a milligramme; on the addition of a large proportion of chloride of ammonium the loss rose to about ·002 grm. The correction for the solubility of the precipitate in the ammoniacal filtrate containing excess of magnesia mixture is ·001 grm. of $2MgO,NH_4O,AsO_5 + aq.$ for 30 c.c.

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[*] If it is dried in a water-bath, the drying must be extremely prolonged, or otherwise more than 1 aq. will be left. After brief drying in the water-bath the compound contains between 1 and 3 eq. water. If it is dried between 105° and 110°, part of the 1 eq. water is lost.

[†] His Handbuch der anal. Chem. 6 Aufl. 2, 390.

[‡] Zeitschr. f. anal. Chem. 2, 19.

[§] *Ib.* 10, 63.

b. Preceded by Precipitation as Arsenio-molybdate of Ammonia.

Mix the acid solution, which must be free from phosphoric and silicic acids, with an excess of solution of molybdate of ammonia. The molybdate of ammonia solution should have been previously mixed with nitric acid in excess, and the whole process is conducted exactly as in the case of phosphoric acid—see § 134, *b*, *β*. After dissolving the arsenio-molybdate in ammonia, neutralize the latter partially with hydrochloric acid. Treat the arseniate of magnesia and ammonia as in *a*. Results satisfactory.

3. *Estimation as Arseniate of Uranium.*

This method was first proposed by WERTHER.* It has been carefully studied by PULLER† in my laboratory and gives thoroughly satisfactory results. Mix the arsenic acid solution with potash or ammonia in excess and then a good excess of acetic acid. (If a precipitate of arseniate of iron or alumina here remains insoluble the method would be inapplicable.) Add acetate of uranium in excess and boil. Wash the slimy precipitate of arseniate of uranium or arseniate of uranium and ammonia by decantation with boiling water and then transfer to a filter. The addition of a few drops of chloroform to the partly cool fluid will hasten the deposition of the precipitate. Dry, transfer the precipitate to a watch-glass, cleaning the filter as much as possible, saturate the latter with nitrate of ammonia, dry it, incinerate in a porcelain crucible, and add the precipitate. If the precipitate contains ammonia, heat very cautiously, finally adding nitric acid, or ignite in oxygen. (See 2, *a*.) If the precipitate is free from ammonia, ignite in the ordinary way. Ammonia salts do not interfere. Properties of the precipitate and residue, § 92, *e*.

4. *Estimation as Tersulphide of Arsenic.*

a. In solutions of Arsenious Acid or Arsenites free from Arsenic Acid.

The solution should be strongly acid with hydrochloric acid. Precipitate with sulphuretted hydrogen and expel the excess with carbonic acid. Pass the latter through the solution for an hour, a longer time is useless. (See § 125, 1.) Wash the precipitate thoroughly and dry at 100° till the weight is constant. Particles of the precipitate which adhere so firmly to the glass that they cannot be removed mechanically are dissolved in ammonia and reprecipitated with hydrochloric acid. Properties of the precipitate, § 92. Do not omit to test a weighed portion to see whether it completely volatilizes on heating. If a residue remains it is to be weighed and the proportional quantity deducted from the total weight of the precipitate. Results accurate.

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* Journ. f. prakt. Chem. 43, 346.

† Zeitschr. f. analyt. Chem. 10, 72.

If the solution contains any substance which decomposes sulphuretted hydrogen, such as sesquichloride of iron, chromic acid, &c., the precipitate produced in the cold contains an admixture of finely divided sulphur. It should be collected in the same manner on a filter dried at 100° and weighed, washed and dried. Extract the admixed sulphur with purified bisulphide of carbon (which should leave no residue on evaporation), continuing till the fluid which runs through leaves no residue. Dry at 100° till the weight is constant. From experiments made in my laboratory it appears that the results thus obtained are quite accurate, even when the amount of admixed sulphur is large; but the precipitation must have been effected in the cold. If on the contrary heat is used, the sulphur is in the form of small agglutinated grains and cannot be completely extracted by cold bisulphide of carbon on the filter. However, it may be extracted by removing the precipitate from the filter and repeatedly digesting it with the bisulphide on a water-bath (PULLER*).

Instead of purifying the sulphide of arsenic you may estimate the arsenic in the mixture of the sulphide with sulphur as follows:—Dissolve the precipitate in strong potash, and pass chlorine into the solution (§ 148, II. 2, *b*). The arsenic and the sulphur are converted into arsenic and sulphuric acid respectively; the former may be estimated according to 2, *a*, or the latter according to § 132. In the latter case, deduct the sulphur found from the weight of the arsenical precipitate. There is no loss of arsenic in this process from volatilization of the chloride, as the solution remains alkaline. The object may also be conveniently attained by the use of nitric acid. A very strong fuming acid, of 86° boiling point, is employed; an acid of 1·42 sp. gr. which boils at a higher temperature does not answer the purpose, as the separated sulphur would fuse, and its oxidation would be much retarded. The well dried precipitate is shaken into a small porcelain dish, treated with a tolerably large excess of the fuming nitric acid, the dish immediately covered with a clock-glass, and as soon as the turbulence of the first action has somewhat abated, heated on a water-bath, till all the sulphur has disappeared, and the nitric acid has evaporated to a small volume. The filter to which the unremovable traces of sulphide of arsenic adhere is treated separately in the same manner, the complete destruction of the organic matter being finally effected by *gently* warming the somewhat dilute solution with chlorate of potassa (BUNSEN†). Or the filter may instead be extracted with ammonia, the solution evaporated in a separate dish, and the residual tersulphide treated as above. In the mixed solution the arsenic acid is finally precipitated as arseniate of magnesia and ammonia (§ 127, 2 *a*).

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* Zeitschr. f. anal. Chem. 10, 46 et seq.

† Annal. d. Chem. u. Pharm. 106, 10.

Treatment of the impure precipitate with ammonia, whereby the sulphide is dissolved, and the sulphur is supposed to remain behind, only gives approximate results, as the ammoniacal solution of tersulphide of arsenic takes up a little sulphur.

b. In solutions of Arsenic Acid, or of a mixture of the two Oxides of Arsenic.

Heat the solution in a flask (preferably on an iron plate) to about 70°, and conduct sulphuretted hydrogen at the same time into the fluid, as long as precipitation takes place. The precipitate formed is always a mixture of sulphur and tersulphide of arsenic, since the arsenic acid is first reduced to arsenious acid with separation of sulphur, and then the former is decomposed (H. ROSE*). Only in the case when a sulphosalt containing pentasulphide of arsenic is decomposed with an acid, is the precipitate actually pentasulphide, and not merely a mixture of sulphur with tersulphide (A. FUCHS†). To convert this mixture of tersulphide of arsenic and granular sulphur into pure tersulphide, suitable for weighing, treat it as follows:—Extract the washed and still moist precipitate on the filter with ammonia, wash the residual sulphur, precipitate the solution with hydrochloric acid without heat, filter, dry, extract with bisulphide of carbon, dry at 100°, and weigh. Results accurate. The mixture of tersulphide of arsenic and sulphur obtained by hot precipitation may, of course, also be estimated directly or indirectly after one of the other methods in 4, *a*.

5. *Volumetric Methods.*

a. Methods which presuppose the presence of Arsenious Acid.

1. FR. MOHR'S method.‡ This method is based upon the same principle as the one given for teroxide of antimony in § 125, 3, *a*, *i.e.*, conversion of arsenious acid in alkaline solution into arsenic acid by solution of iodine ($AsO_3 + 2NaO + 2I = AsO_5 + 2NaI$).

If, therefore, you have arsenious acid or an alkaline arsenite in aqueous solution, mix a weighed or measured quantity of the fluid, containing about ·1 grm. AsO_3, with 20 c.c. of a saturated solution of bicarbonate of soda (purified by washing with water); add some starch-paste, then standard solution of iodine (§ 146), until the iodide of starch reaction just makes its appearance; reckon for every 2 eq. iodide used 1 eq. arsenious acid. If the solution of arsenious acid is acid, you must first neutralize it with pure carbonate of soda, if alkaline, with pure hydrochloric acid, before proceeding to add the bicarbonate of soda. Of course, the solution must contain no substances which act upon solution of iodine (SO_2,S_2O_2). The results are accurate, compare Expt. No. 79, also WAITZ.§

2. KESSLER'S method.‖ This is based on the same principle as the method given for antimony, § 125, 3, *b*, viz., upon the oxidation of the arsenious acid in hydrochloric solution to arsenic acid with bichromate of potash.¶ The process is exactly similar. The results are only

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* Pogg. Annal. 107, 186.

† Zeitschr. f. anal. Chem. 1, 189.

‡ His Lehrbuch der Titrirmethode, 3 Aufl. 275.

§ Zeitschr. f. anal. Chem 10, 162. WAITZ'S attempts to convert the arsenic in the tersulphide into alkaline arsenite were not successful.

‖ Pogg. Annal. 95, 204; 113, 134; 118, 17; Zeitschr. f. anal. Chem. 2, 383.

¶ Permanganate of potash may also be used, excess being added, and the latter being estimated with iron. However, the permanganate should only be used for trustworthy when at least one-sixth of the volume of the fluid consists of hydrochloric acid of 1·12 sp. gr. However, the hydrochloric acid should not exceed half the volume of the fluid, or the end-reaction depending on the formation of ferricyanide of iron will be slower in making its appearance, and will lose its sharpness.

If for any reason the direct titration of the hydrochloric solution is impracticable, precipitate with sulphuretted hydrogen (at 70° in the presence of arsenic acid), wash the precipitate, transfer it with the filter to a stoppered bottle, and treat with a nearly saturated solution of chloride of mercury in hydrochloric acid of 1·12 sp. gr., digest with the stopper firmly fixed at a gentle heat, till the precipitate has become white, dilute with a measured quantity of water (not allowing the proportion of hydrochloric acid to fall below one-sixth), add the bichromate, then the iron solution, and proceed generally according to § 125, 3, *b*. Results good. Compare also WAITZ.*

3. BUNSEN's method.† This method is based upon the following facts:—

aa. If bichromate of potassa is boiled with concentrated hydrochloric acid, 3 eq. chlorine are disengaged to every 2 eq. chromic acid ($2CrO_3 + 6HCl = Cr_2Cl_3 + 3Cl + 6HO$).

bb. But if arsenious acid is present (not in excess) there is not the quantity of chlorine disengaged corresponding to the chromic acid, but so much less of that element as is required to convert the arsenious into arsenic acid ($AsO_3 + 2Cl + 2HO = AsO_5 + 2HCl$). Consequently, for every 2 eq. chlorine wanting is to be reckoned 1 eq. arsenious acid.

cc. The quantity if chlorine is estimated by determining the quantity of iodine liberated by it from iodide of potassium.

These are the principles of BUNSEN's method. For the manner of execution I refer to the Estimation of Chromic Acid.

b. Method, which presupposes the presence of Arsenic Acid.

This method depends on the precipitation of the arsenic acid by uranium solution and the recognition of the end of the reaction by means of ferrocyanide of potassium. It is therefore the same as was suggested for phosphoric acid by LECOMTE, and brought into use by NEUBAUER,‡ and afterwards by PINCUS.§

BÖDEKER,‖ who first employed the process for arsenic acid, recommends the employment of a solution of nitrate of sesquioxide of uranium, as this is more permanent than the hitherto used acetate, which is gradually decomposed by the action of light.

The uranium solution has the correct degree of dilution, if it contains about 20 grm. sesquioxide of uranium in 1 litre. It should contain as little free acid as possible. The determination of its value may be effected with the aid of pure arseniate of soda or by means of arsenious acid,—the latter is converted into arsenic acid by boiling with fuming nitric acid. The solution is rendered strongly alkaline with ammonia, and then distinctly acid with acetic acid. The uranium solution is now run in from the burette slowly, the liquid being well stirred all the while, till a drop of the mixture spread out on a porcelain

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sulphuric acid solutions of arsenious acid. Compare WAITZ, Zeitschr. f. anal. Chem. 10, 174.

* Zeitschr. f. anal. Chem. 10, 169.

† Annal. d. Chem. u. Pharm. 86, 290.

‡ Archiv fur wissenschaftliche Heilkunde, 4, 228.

§ Journ. f. prakt. Chem. 76, 104.

‖ Annal. d. Chem. u. Pharm. 117, 195.

plate, gives with a drop of ferrocyanide of potassium placed in its centre, a distinct reddish-brown line where the two fluids meet. The height of the fluid in the burette is nôw read off, the level of the mixture in the beaker is marked with a strip of gummed paper, and the beaker is emptied and washed, filled with water with addition of about as much ammonia and acetic acid as was before employed, and the uranium solution is cautiously dropped in from the burette, till a drop taken out of the beaker and tested as above, gives an equally distinct reaction. The quantity of uranium solution used in this last experiment is the excess, which must be added to make the end-reaction plain for the dilution adopted. This amount is subtracted from that used in the first experiment, and we then know the exact value of the uranium solution with reference to arsenic acid.

In an actual analysis, the arsenic is first brought into the form of arsenic acid, a clear solution is obtained containing acetate of ammonia and some free acetic acid,* and the process is conducted exactly as in determining the value of the standard solution. The experiment to ascertain the correction must not be omitted here, otherwise errors are sure to arise from the different degrees of dilution of the arsenic acid solutions used in the determination of the value of the standard solution and in the actual analyses. The results of two determinations of arsenic given by BÖDEKER are satisfactory. To execute the method well requires practice. The results are not exact enough unless the conditions as regards amount and quality of alkali salts are nearly similar in the standardizing of the uranium solution and in its use. Compare WAITZ.†

6. *Estimation of Arsenious Acid by Indirect Gravimetric Analysis.*

a. ROSE's method. Add to the hydrochloric acid solution, in the preparation of which care must be taken to exclude oxidizing substances, a solution of sodio- or ammonio-terchloride of gold in excess, and digest the mixture for several days, in the cold, or, in the case of dilute solutions, at a gentle warmth; then weigh the separated gold as directed in § 123. Keep the filtrate to make quite sure that no more gold will separate. 2 eq. gold correspond to 3 eq. arsenious acid.

b. VOHL's‡ method. Mix the solution with a weighed quantity of bichromate of potassa, and free sulphuric acid; estimate the chromic acid still present by the method given in § 130, *c*, and deduce from the quantity of that acid consumed in the process, *i.e.*, reduced by the arsenious acid, the quantity of the latter, after the formula $3AsO_3 + 4CrO_3 = 3AsO_5 + 2Cr_2O_3$.

Supplement to the Sixth Group.

§ 128.

8. MOLYBDIC ACID.

Molybdic acid is converted, for the purpose of its estimation, either into binoxide of molybdenum, or into molybdate of lead, or into bisulphide of molybdenum.

a. Pure molybdic acid (MoO_3), and also molybdate of ammonia, may be reduced to binoxide by heating in a current of hydrogen gas. This may be done either in a porcelain boat, placed in a wide glass tube, or in a platinum or porcelain crucible with perforated cover (§ 108, fig. 79). The operation is continued till the weight remains constant. The temperature must not exceed a gentle redness, otherwise the binoxide itself might lose oxygen and become partially converted into metal. In the case of molybdate of ammonia the heat must be very low at first on account of the frothing. If you have a platinum tube it is safer to ignite the molybdic acid in this for 2 or 3 hours in a slow current of hydrogen, thus reducing it to the metallic state. When reducing to binoxide the contents of the crucible are frequently gray below, and brown above (RAMMELSBERG*).

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* Alkalies, alkaline earths and oxide of zinc may be present, but not such metals as yield colored precipitates with ferrocyanide of potassium, as, for instance, copper.

† Zeitschr. f. anal. Chem. 10, 182.

‡ Annal. d. Chem. u. Pharm. 94, 219.

b. The following is the best method of precipitating molybdic acid from an alkaline solution. Dilute the solution, if necessary, neutralize the free alkali with nitric acid, and allow the carbonic acid, which may be liberated in the process, to escape, then add neutral nitrate of suboxide of mercury. The yellow precipitate formed appears at first bulky, but after several hours' standing it shrinks; it is insoluble in the fluid, which contains an excess of nitrate of suboxide of mercury. Collect on a filter, and wash with a dilute solution of nitrate of suboxide of mercury, as it is slightly soluble in pure water. Dry, remove the precipitate as completely as practicable from the filter, and determine the molybdenum in it as directed in *a* (H. ROSE); or mix the precipitate, together with the filter-ash, with a weighed quantity of ignited oxide of lead, and ignite until all the mercury is expelled; then add some nitrate of ammonia, ignite again and weigh. The excess obtained, over and above the weight of the oxide of lead used, is molybdic acid (SELIGSOHN†).

c. CHATARD‡ recommends estimating molybdic acid in the solution of its alkali salts by adding acetate of lead in slight excess to the boiling solution and boiling for a few minutes. The precipitate which is at first milky becomes granular, deposits well and may be easily washed with hot water. It is dried, removed from the filter as much as possible, ignited and weighed as PbO,MoO_3. The method is only applicable for solutions of *pure* alkaline molybdates.

d. The precipitation of molybdenum as sulphide is always a difficult operation. If the acid solution is supersaturated with sulphuretted hydrogen, warmed, and filtered, the filtrate and washings are generally still colored. They must, accordingly, be warmed, and sulphuretted hydrogen again added, and the operation must afterwards, if necessary, be repeated until the washings appear almost colorless. The precipitation succeeds better when the sulphide of molybdenum is dissolved in a relatively large excess of sulphide of ammonium, and, after the fluid has acquired a reddish-yellow tint, precipitated with hydrochloric acid. ZENKER§ advises then to boil, until the sulphuretted hydrogen is expelled, and to wash with hot water, at first slightly acidified. To make quite sure that all the molybdenum is precipitated, treat the filtrate and washings again with sulphuretted hydrogen and allow to stand for some time. The brown sulphide of molybdenum is collected on a weighed filter, and the molybdenum determined in an aliquot part of it, by gentle ignition in a current of hydrogen gas, as in *a*. The brown sulphide of molybdenum changes in this process to the gray bisulphide (H. ROSE).

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* Pogg. Annal. 127, 281; Zeitschr. f anal. Chem. 5, 203.

† Journ. f. prakt. Chem. 67, 472.

‡ Sill. Amer. Journ. (3), 1, 416.

§ Journ. f. prakt. Chem. 58, 259.

e. F. PISANI* gives the following method for estimating molybdic acid volumetrically. Digest the molybdic acid with hydrochloric acid and zinc, dissolving any precipitate which may form from want of acid and also the excess of zinc. Convert the solution of sesquioxide of molybdenum thus obtained into molybdic acid by standard permanganate of potash. The brown color of the solution turns first green, and then disappears. RAMMELSBERG† confirms the statements of PISANI.

II. DETERMINATION OF ACIDS IN COMPOUNDS CONTAINING ONLY ONE ACID, FREE OR COMBINED;—AND SEPARATION OF ACIDS FROM BASES.

FIRST GROUP.

First Division.

ARSENIOUS ACID—ARSENIC ACID—CHROMIC ACID—(Selenious Acid, Sulphurous and Hyposulphurous Acids, Iodic Acid).

§ 129.

1. ARSENIOUS AND ARSENIC ACIDS.

These have been already treated of among the bases (§ 127) on account of their behavior with sulphuretted hydrogen; they are merely mentioned here to indicate the place to which they properly belong. The methods of separating them from the bases will be found in Section V.

§ 130.

2. CHROMIC ACID.

I. DETERMINATION.

Chromic acid is determined either as *sesquioxide of chromium*, *chromate of lead*, or *chromate of baryta* But it may be estimated also from the quantity of carbonic acid disengaged by its action upon oxalic acid in excess, and also by volumetric analysis. In employing the first method, it must be borne in mind that 1 eq. sesquioxide of chromium corresponds to 2 eq. chromic acid.

a. Determination as Sesquioxide of Chromium.

α. The chromic acid is reduced to the state of sesquioxide, and the amount of the latter determined (§ 106). The reduction is effected either by heating the solution with hydrochloric acid and alcohol; or by mixing hydrochloric acid with the solution, and conducting sulphuretted hydrogen into the mixture; or by adding a strong solution of sulphurous acid, and applying a gentle heat. With concentrated solutions the first method is generally resorted to, with dilute solutions one of the two latter. With respect to the first method, I have to remark that the alcohol must be expelled before the sesquioxide of chromium can be precipitated with ammonia; and with respect to the second, that the solution supersaturated with sulphuretted hydrogen must be allowed to stand in a moderately warm place, until the separated sulphur has completely subsided. The results are accurate, unless the weighed precipitate contains silica and lime, which is always the case if the precipitation is effected in glass vessels.

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* Compt. rend. 59, 301.

† Pogg. Annal. 127, 281; Zeitschr. f. anal. Chem. 5, 203.

β. The neutral or slightly acid (nitric acid) solution is precipitated with nitrate of suboxide of mercury, after long standing the red precipitate of chromate of suboxide of mercury is filtered off, washed with a dilute solution of nitrate of suboxide of mercury, dried, ignited, and the residuary sesquioxide of chromium weighed (H. Rose). Results accurate.

b. Determination as Chromate of Lead.

The solution is mixed with acetate of soda in excess, and acetic acid added until the reaction is strongly acid; the solution is then precipitated with neutral acetate of lead. The washed precipitate is either collected on a weighed filter, dried in the water-bath, and weighed; or it is gently ignited as directed § 53, and then weighed. For the properties of the precipitate, see § 93, 2. Results accurate.

c. Determination as Chromate of Baryta.

Mix the solution of the alkaline chromate with acetic acid to moderately acid reaction, add chloride of barium in slight excess, allow the fine precipitate twelve hours to subside, wash with acetate of ammonia as far as possible by decantation, displace the acetate of ammonia by solution of nitrate of ammonia (or the chromic acid may be partially reduced on igniting), dry, remove as much as possible from the filter, and ignite gently. Properties of the precipitate, § 93, 2, *c* (H. Rose, Pearson*). The test analyses given by Pearson are satisfactory.

d. Determination by means of Oxalic Acid (after Vohl).

When chromic acid and oxalic acid are brought together, the former yields oxygen to the latter: sesquioxide of chromium is formed, and carbonic acid escapes ($2CrO_3 + 3C_2O_3 = Cr_2O_3 + 6CO_2$). Three eq. carbonic acid (66) correspond accordingly to one eq. chromic acid (50·24). The process is the same as in the analysis of manganese ores (§ 230). 1 part of chromic acid requires 2¼ parts of oxalate of soda. If it is intended to determine in the residue the alkali which was combined with the chromic acid, oxalate of ammonia is used.

e. Determination by Volumetric Analysis.

α. Schwarz's method.

The principle of this very accurate method is identical with that upon which Penny's method of determining iron is based (§ 112, 2, *b*). The execution is simple: acidify the not too dilute solution of the chromate with sulphuric acid, add in excess a measured quantity of solution of protoxide of iron, the strength of which you have previously ascertained, according to the directions of § 112, 2, *a*, or *b*, or the solution of a weighed quantity of sulphate of iron and ammonia, free from sesquioxide, and then determine in the manner directed § 112, 2, *a*, or *b*, the quantity of protoxide of iron remaining. The difference shows the amount of iron that has been converted by the chromic acid from the state of protoxide to that of sesquioxide. 1 grm. of iron corresponds to 0·5981 of chromic acid. To determine the chromic acid in chromate of lead, the latter is, after addition of the sulphate of protoxide of iron and ammonia, most thoroughly triturated with hydrochloric acid, water added, and the analysis then proceeded with.

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* Amer. Journ of Science (2), 45, 298; Zeitschr. f. anal. Chem. 9, 108.

β. Bunsen's method.*

If a chromate is boiled with an excess of fuming hydrochloric acid, there are disengaged for every 2 eq. chromic acid 3 eq. chlorine; for instance, $KO,2CrO_3 + 7HCl = KCl + Cr_2Cl_3 + 7HO + 3Cl$. If the escaping gas is conducted into solution of iodide of potassium in excess, the 3 eq. chlorine set free 3 eq. iodine. By determining the quantity of the latter element in the manner described in § 146, we find the quantity of the chromic acid; 380·55 of iodine corresponding to 100·48 of chromic acid.

The analytical process is conducted as follows:—Put the weighed sample of the chromate (say ·3 to ·4 grm.) into the little flask *d*, fig. 85 (blown before the lamp, and holding only from 36 to 40 c.c.), and fill the flask two-thirds with pure fuming hydrochloric acid (free from Cl and SO_2), add a compact lump of magnesite, to keep up a constant current of gas and prevent the fluid from receding. Connect the bulbed evolution tube *a* with the neck of the flask by means of a stout india-rubber tube *c*. As shown in the engraving, *a* is a bent pipette, drawn out, at the lower end, into an upturned point. A loss of chlorine need not be apprehended on adding the hydrochloric acid, as the disengagement of that gas begins only upon the application of heat. Insert the evolution tube into the neck of the retort, which is one-third filled with solution of iodide of potassium.† This retort holds about 160 c.c. The neck presents two small expansions, blown before the lamp, and intended, the lower one, to receive the liquid which is forced up during the operation, the upper one, to serve as an additional guard against spirting. Apply heat now, cautiously, to the little flask. After two or three minutes' ebullition, the whole of the chlorine has passed over, and liberated its equivalent quantity of iodine in the iodide of potassium solution. When the ebullition is at an end, take hold of the caoutchouc tube *c* with the left hand, and, whilst steadily holding the lamp under the flask with the right, lift *a* so far out of the retort that the curved point is in the bulb *b*. Now remove first the lamp, then the flask, dip the retort in cold water to cool it, and shake the fluid in it about to effect

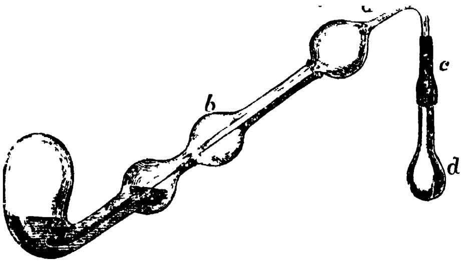

Fig. 85.

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* Annal. d. Chem. u. Pharm. 86, 279.

† 1 part of pure iodide of potassium, free from iodic acid, dissolved in 10 parts of water. The fluid must show no brown tint immediately after addition of dilute sulphuric acid.

the complete solution of the separated iodine in the excess of iodide of potassium solution. When the fluid is quite cold, transfer it to a beaker, rinsing the retort into the beaker, and proceed as directed § 146. The method gives very satisfactory results. The apparatus here recommended differs slightly from that used by Bunsen, the retort of the latter having only one bulb in the neck, and the evolution tube no bulb, being closed instead, at the lower end, by a glass or caoutchouc valve, which permits the exit of the gas from the tube, but opposes the entrance of the fluid into it. I think the modifications which I have made in Bunsen's apparatus are calculated to facilitate the success of the operation. Instead of this apparatus that described § 142 may also be very conveniently used.

γ. There is a method by Rube* depending on the reaction: $2CrO_3 + 6K_2Cfy + 6HCl = 3KCl + Cr_2Cl_3 + 3K_3Cfdy + 6HO$. Also one by Zulkowsky† which depends on the estimation of the iodine separated directly by chromic acid—*i.e.* without distillation; the process is exactly similar to that given p., 227, β.

II. Separation of Chromic Acid from the Bases.

a. Of the First Group.

α. Reduce the chromic acid as directed in I., and separate the sesquioxide of chromium from the alkalies as directed in § 155.

β. Mix the chromate of potassa or soda with about 5 parts of dry pulverized chloride of ammonium, and heat the mixture cautiously. The residue contains the chlorides of the alkali metals and sesquioxide of chromium, which may be separated by means of water.

γ. Precipitate the chromic acid according to I., *a*, β, and separate the mercury and alkali in the filtrate by § 162.

b. Of the Second Group.

α. Fuse the compound with 4 parts of carbonate of soda and potassa, and treat the fused mass with hot water, which dissolves the chromic acid in the form of an alkaline chromate. The residue contains the alkaline earths in the form of carbonates; but as they contain alkali, they cannot be weighed directly. The chromic acid in the solution is determined as in I. Chromates of strontia and lime may be decomposed by boiling with carbonate of potassa or soda. Chromate of baryta may also be decomposed in the same way, but the boiling must be repeated a second time with fresh solution of alkaline carbonate (H. Rose).

β. Dissolve in hydrochloric acid, reduce the chromic acid according to I., *a*, and separate the sesquioxide of chromium from the alkaline earth according to § 156.

γ. Chromate of magnesia as well as other chromates of the alkaline earths soluble in water may be easily decomposed also, by determining the chromic acid according to I., *a*, β, or I., *b*, and separating the magnesia, &c., in the filtrate from the excess of the salt of mercury or lead as directed § 162.

δ. Chromates of baryta, strontia, and lime may also be decomposed by the method described II., *a*, β. Compare Bahr, Analysis of bichromate of baryta, lime, &c.* H. ROSE recommends igniting the finely powdered substance with five parts of chloride of ammonium. One ignition usually suffices to decompose the substance completely, but it is better to repeat the ignition with chloride of ammonium, to make sure that the weight remains constant before separating the chloride of barium, &c., from the residual oxide of chromium by water.

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* Journ. f. prakt. Chem. 95, 53; Zeitschr. f. anal. Chem 4, 444.

† Journ. f. prakt. Chem. 103, 351; Zeitschr. f. anal. Chem. 8, 74.

c. OF THE THIRD GROUP.

a. *From Alumina.*

If you have chromic acid to separate from alumina in acid solution, precipitate the alumina with ammonia or carbonate of ammonia (§ 105, *a*), and determine the chromic acid in the filtrate according to I. If the washed alumina has a yellow color, treat on the filter with ammonia, and wash with boiling water; this will remove the last traces of chromic acid. However, a little alumina dissolves in the ammonia, therefore heat the ammoniacal fluid in a platinum dish till it has almost lost its alkaline reaction, and filter the flocks of alumina which separate to the principal precipitate.

β. *From Sesquioxide of Chromium.*

aa. Determine in one portion the quantity of the chromic acid according to I., *d*, or I., *e*, *a*, or *β*, and in another portion the total amount of the chromium, by converting it into sesquioxide by cautious ignition with chloride of ammonium, or by I., *a*, or by converting it entirely into chromic acid by § 106, 2.

bb. In many cases the chromic acid may be precipitated according to I., *a*, *β*, or I., *b*. The sesquioxide of chromium and suboxide of mercury, or oxide of lead, in the filtrate, are separated as directed § 162.

cc. The hydrated compounds of sesquioxide of chromium with chromic acid, such as are obtained by precipitating a solution of sesquioxide of chromium with a solution of chromate of potassa, &c., may also be analysed by ignition in a stream of dry air, in a bulb tube, to which a chloride of calcium tube is attached (fig. 44, § 36). The loss of weight represents the joint amount of oxygen and water that have escaped. If the increment of the CaCl tube is deducted, we shall have the oxygen. Now every 3 eq. oxygen correspond to 2 eq. of chromic acid. The amount of the latter being thus calculated, we have only to subtract its equivalent quantity of sesquioxide from the weight of residue after the ignition, and the remainder is the quantity of sesquioxide originally present. VOGEL† and also STORER and ELLIOT‡ have employed this method.

d. OF THE FOURTH GROUP.

a. Proceed as directed in *b*, *a*. Upon treating the fused mass with hot water, the metals are left as oxides. In the case of manganese the fusion must be effected in an atmosphere of carbonic acid gas. Apparatus, fig. 79 in § 108.

β. Reduce the chromic acid as directed in I., *a*, and separate the sesquioxide of chromium from the metals in question, as directed in § 160.

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* Journ. f. prakt. Chem. 60, 60. † *Ib.* 77, 484.

‡ Proceedings of the American Academy, 5, 198.

e. OF THE FIFTH AND SIXTH GROUPS.

a. Acidify the solution, and precipitate, either at once or after reduction of the chromic acid by sulphurous acid, with sulphuretted hydrogen. The metals of the fifth and sixth groups precipitate in conjunction with free sulphur (§§ 115 to 127), the chromic acid is reduced. Filter and determine the sesquioxide of chromium in the filtrate, as directed in I., *a*.

β. Chromate of lead may be conveniently decomposed by heating with hydrochloric acid and some alcohol; the chloride of lead and sesquichloride of chromium formed are subsequently separated by means of alcohol (compare § 162). The alcoholic solution ought always to be tested with sulphuric acid; should a precipitate of sulphate of lead form, this must be filtered off, weighed, and taken into account (compare also § 130, I., *d*).

Supplement to the First Division.

§ 131.

1. SELENIOUS ACID.

From aqueous or hydrochloric acid solutions of selenious acid, the selenium is precipitated by sulphurous acid gas or, in presence of an excess of acid, by sulphite of soda, or sulphite of ammonia. The precipitated liquid is heated to boiling for ¼ hour, which changes the precipitate from its original red color to black, and makes it dense and heavy. The liquid is tested by a further addition of the reagent to see whether any more selenium will separate; the precipitate is finally collected on a weighed filter, dried at a temperature somewhat below 100°, and weighed. Since H. ROSE* has shown that the presence of hydrochloric acid is an essential condition to the complete reduction of the selenious acid, the former acid must be added, if not already present. To make quite sure that all the selenium has been removed, the filtrate is evaporated to a small volume, with addition of chloride of potassium or chloride of sodium, boiled with strong hydrochloric acid, so as to reduce any selenic acid to selenious acid, and tested once more with sulphurous acid. If the solution contains nitric acid it must be evaporated repeatedly with hydrochloric acid, with addition of chloride of sodium or chloride of potassium. If the latter were omitted there would be considerable loss of selenious acid (RATHKE†).

As regards the separation of selenious acid from the bases, the following brief directions will suffice:—

a. If the bases are not liable to be altered by the action of sulphurous acid and hydrochloric acid, the selenium may be at once precipitated in the way just given; the filtrate, when evaporated with sulphuric acid, yields the base as sulphate.

b. From bases which are not thrown down from acid solution by hydrosulphuric acid, the selenious acid may be separated by sulphuretted hydrogen. The precipitate (according to RATHKE‡, a mixture of SeS_2, Se_2S and S), contains 2 eq. sulphur to 1 eq. selenium. If it is dried at or a little below 100°, the weight of the selenium may be accurately ascertained. Should, however, extra sulphur be mixed with the precipitate, the latter is oxidized while still moist with hydrochloric acid and chlorate of potassa, or by treatment with potassa solution with simultaneous heating and transmission of chlorine. It is necessary here to oxidize the sulphur completely, as it may enclose selenium. The solution now containing selenic acid is heated till it smells no longer of chlorine, hydrochloric acid is added, and the mixture is reheated. The selenic acid is hereby reduced to selenious acid, and when the solution has again ceased to smell of chlorine, the selenium is precipitated with sulphurous acid. Instead of this process you may digest the precipitate of sulphur and selenium for some hours with concentrated cyanide of potassium, which will completely dissolve it, and then throw down the selenium from the dilute solution with hydrochloric acid as in *c* (RATHKE, *loc. cit.*).

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* Zeitschr. f. anal. Chem. 1, 73.

† Journ. f. prakt. Chem. 108, 249; Zeitschr. f. anal. Chem. 9, 484.

‡ Journ. f. prakt. Chem. 108, 252.

c. In many selenites or selenates the selenium may also be determined, by converting first into selenocyanide of potassium, and precipitating the aqueous solution of the latter with hydrochloric acid (OPPENHEIM*). To this end the substance is mixed with 7 or 8 times its quantity of ordinary cyanide of potassium (containing cyanic acid), the mixture is put into a long-necked flask, or a porcelain crucible, covered with a layer of cyanide of potassium, and fused in a stream of hydrogen. The temperature is kept so low that the glass or porcelain is not attacked, and while cooling care must be taken to exclude atmospheric air. When cold, the brown mass is treated with water, and the colorless solution filtered, if necessary. The liquid should be somewhat but not immoderately diluted. Now boil some time (in order to convert the small quantity of selenide of potassium that may be present into selenocyanide of potassium by the excess of cyanide of potassium), allow to cool, supersaturate with hydrochloric acid, and heat again for some time. At the end of 12 or 24 hours all selenium will have separated, filter, dry at 100°, and weigh. The results obtained by this process are accurate (H. ROSE†). If the selenium agglomerates together on heating, it may enclose salts. In such cases, by way of control, it should be redissolved in nitric acid, and, after addition of hydrochloric acid, precipitated with sulphurous acid. The fluid filtered from the selenium precipitate is, as a rule, free from selenium; it is, however, always well to satisfy one's self on this point by the addition of sulphurous acid

d. From many bases the selenious acid (and also the selenic acid) may be separated by fusing the compound with 2 parts of carbonate of soda and 1 part of nitrate of potassa, extracting the fused mass thoroughly by boiling with water, saturating the filtrate, if necessary, with carbonic acid, to free it from lead which it might contain, then boiling down with hydrochloric acid in excess (to reduce the selenic acid and drive off the nitric acid), and precipitating finally with sulphurous acid.

Selenium, if pure, must volatilize without residue when heated in a tube.

2. SULPHUROUS ACID.

To estimate free sulphurous acid in a fluid which may contain also other acids (sulphuric acid, hydrochloric acid, acetic acid), a weighed quantity of the fluid is diluted with water, absolutely free from air,‡ until the diluted liquid contains not more than ·05 per cent. by weight of sulphurous acid; the solution is poured with stirring into an excess of standard solution of iodine, the free iodine remaining is titrated with hyposulphite, and the iodine used for the oxidation of the sulphurous acid is thus found. The equation is $I + 2HO + SO_2 = HI + HO,SO_3$. According to FINKENER, if the iodine is added to the sulphurous acid the reaction is not quite normal. Anyhow this method of operating prevents any loss of sulphurous acid. For the details, see § 146. In the case of sulphites soluble in water or acids, water perfectly free from air is poured over the substance, in sufficient quantity to attain the degree of dilution stated above, sulphuric or hydrochloric acid is added in excess, and then the titration is effected as above. The greatest care must be taken in this method, to use, for the purpose of dilution, water absolutely free from air.

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* Journ. f. prakt. Chem. 71, 280.

† Zeitschr. f. anal. Chem. 1, 73.

‡ Prepared by long-continued boiling and subsequent cooling with exclusion of air.

Sulphurous acid may also be determined in the gravimetric way, by conversion into sulphuric acid, and precipitation of the latter with baryta, according to § 132. This method is especially applicable in the case of sulphites quite free from sulphuric acid. The conversion of the sulphurous into sulphuric acid is effected in the wet way, best by pouring the dilute solution with stirring into excess of chlorine or bromine water. Sulphites insoluble in water are decomposed by boiling with carbonate of soda and the solution of sulphite of soda is treated as directed. After driving off the excess of chlorine or bromine by heating, the moderately acid solution is precipitated with chloride of barium. Sulphites may be oxidized in the dry way by heating in a platinum crucible, with 4 parts of a mixture of equal parts carbonate of soda and nitrate of potassa.

3. HYPOSULPHUROUS ACID.

Hyposulphurous acid, in form of soluble hyposulphites, may be determined by means of iodine, in a similar way to sulphurous acid. The reaction is represented by the equation, $2(NaO,S_2O_2) + I = NaO, S_4O_5 + NaI$. The salt under examination is dissolved in a large amount of water, starch-paste added, and then the neutral solution is titrated with iodine. That this method can give correct results only in cases where no other substances acting upon iodine are present, need hardly be mentioned. Hyposulphurous may like sulphurous acid be converted into sulphuric acid by means of chlorine or bromine water, and then determined.

4. IODIC ACID.

Iodic acid may be determined by the following easy method:—distil the acid, in the free state or in combination with a base, with an excess of pure fuming hydrochloric acid, in the apparatus described in § 130, *c*, *β* (chromic acid), receive the disengaged chlorine in solution of iodide of potassium, and determine the separated iodine as directed in § 130, *c*, *β*. As 1 eq. iodic acid sets free 4 eq. chlorine, and consequently 4 eq. iodine, you have to reckon 166·85 of iodic acid for 507·4 of iodine. The decomposition of iodic acid by hydrochloric acid is represented by the equation $IO_5 + 5HCl = ICl + 5HO + 4Cl$ (BUNSEN*). The following method also yields good results. Mix the solution with dilute sulphuric acid, add iodide of potassium in excess, and determine the amount of liberated iodine, after § 146. One-sixth of the iodine thus found is derived from the iodic acid ($IO_5 + 5HI = 5HO + I_6$). See RAMMELSBERG.*

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* Annal. d. Chem. u. Pharm. 86, 285.

5. NITROUS ACID.

The nitrous acid in nitrites which are free from nitrates may be estimated by converting the nitrogen into ammonia and determining the latter, or by determining the oxidizing action on protosalt of iron. This method is conducted exactly as described under nitric acid (§ 149). When nitric acid is also present, nitrous acid may be determined very satisfactorily with a solution of pure permanganate of potassa, provided the fluid be sufficiently diluted to prevent the nitrous acid, which is liberated by the addition of a stronger acid, being decomposed by water with formation of nitric acid and nitric oxide. For 1 part of anhydrous nitrous acid, at least 5000 parts of water should be present. The decomposition is represented by the following equation :—$5NO_3 + 2Mn_2O_7 = 5NO_5 + 4MnO$. If the permanganate be standardized with iron dissolved to protoxide, 4 eq. iron correspond to 1 eq. NO_3, since both of these require 2 eq. oxygen. Nitrites are dissolved in *very slightly* acidulated water, the permanganate is added till the oxidation of the nitrous acid is nearly completed, the solution is then made strongly acid, and finally permanganate is added to light-red coloration.

To determine hyponitric acid in red fuming nitric acid, transfer a few c.c. to about 500 c.c. cold pure distilled water with stirring, and determine the nitrous acid produced. 1 eq. nitrous acid found corresponds to 2 eq. hyponitric acid, for the latter—when mixed with such a large quantity of water as is indicated above—is decomposed in accordance with the following equation :—$2NO_4 + 2HO = HO,NO_5 + HO,NO_3$ (SIG. FELDHAUS†).

Nitrous and hyponitric acid in presence of nitric acid may also be estimated by the reduction of chromic acid. An excess of standard bichromate of potash is added, and the undecomposed residue of chromic acid is estimated with standard solution of protoxide of iron (F. MOHR‡).

As regards the estimation of nitrous acid with binoxide of lead, comp. FELDHAUS, *loc. cit.* p. 431, also LANG§ and J. LÖWENTHAL‖. Regarding the estimation of nitrous acid in water, see § 205.

Second Division of the First Group of the Acids.

SULPHURIC ACID ; (Hydrofluosilicic Acid).

§ 132.

SULPHURIC ACID.

I. DETERMINATION.

Sulphuric acid is usually determined in the gravimetric way as *sulphate of baryta.* The acid may, however, be estimated also by the acidimetric method (§ 205), and by certain volumetric methods, based upon the insolubility of the sulphate of baryta (and the sulphate of lead).

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* Pogg. Annal. 135, 493 ; Zeitschr. f. anal. Chem. 8, 456.

† Zeitschr. f. anal. Chem. 1, 426.

‡ His Lehrbuch der Titrirmethode, 3 Aufl. 236.

§ Zeitschr. f. anal. Chem. 1, 485.

‖ *Ib.* 3, 176.

1. *Gravimetric Method.*

The exact estimation of sulphuric acid as sulphate of baryta is by no means so simple and easy as it was formerly supposed to be, but requires, on the contrary, great care and attention. This arises from three causes: first, the sulphate of baryta is found to be far more soluble than was imagined in solutions of free acids and of many salts; secondly, it is extremely liable to carry down with it foreign salts, which are of themselves soluble in water; thirdly, when the precipitate has once separated in an impure state, it is often very difficult to purify it completely.

The solution should contain but little free hydrochloric acid, and no nitric or chloric acid. If either of the two last are present, evaporate repeatedly, on the water-bath with pure hydrochloric acid. Dilute considerably, heat nearly to boiling, add chloride of barium in moderate excess, and allow to settle for a long time at a gentle heat. Decant the clear fluid through a filter, treat the precipitate with boiling water, allow to settle, decant again, and so on, till the washings are free from chlorine. Finally transfer the precipitate to the filter, dry and treat according to § 53, using only a moderate red heat.

After the precipitate has been weighed it is well to warm it for some time with dilute hydrochloric acid on the water-bath. Then pour off the hydrochloric acid through a small filter, wash the precipitate by decantation with boiling water without removing it to the filter, evaporate the filtrate and washings nearly to dryness in a platinum or porcelain dish, add water, collect the minute amount of sulphate of baryta here left undissolved upon the small filter, wash, dry, incinerate, add the ash to the bulk of the precipitate, ignite again, and weigh. If the precipitate has lost weight, this shows that it at first contained foreign salts.

This method of purification sometimes fails when the precipitate contains oxide of iron or platinum (CLAUS*), and it invariably fails when the solution contains any notable quantity of nitric acid.† In such cases there is only one resource, namely, to fuse with about four parts of carbonate of soda, warm with water, filter, wash with boiling water, acidify the filtrate slightly with hydrochloric acid, and determine the sulphuric acid again.

The results are thoroughly satisfactory if these directions are attended to; if not, the result may be two or three per-cents too high or too low.

2. *Volumetric Methods.*

a. After CARL MOHR.‡ We require a normal solution of chloride of barium, containing 121·96 grm. of the pure crystallized salt in 1 litre, and also normal nitric or hydrochloric acid and normal soda (§ 215). Add to the fluid to be examined for sulphuric acid—which, should it contain much free acid, is previously to be nearly neutralized with pure carbonate of soda—a measured quantity of chloride of barium solution, best a round number of cubic centimetres, in more than sufficient proportion to precipitate the sulphuric acid, but not in too great excess. Digest the mixture for some time in a warm place, then precipitate, without previous filtration, the excess of chloride of barium with carbonate of ammonia and a little ammonia, filter off the sulphate and carbonate of baryta, wash until the water running off acts no longer upon red litmus paper, and then determine the carbonate of baryta by the alkalimetric method given in § 223. Deduct the c.c. of normal acid used from the c.c. of chloride of barium and the remainder will be the c.c. of chloride of barium corresponding to the sulphuric acid present. The results of this method are quite satisfactory, if the solution does not contain too much free acid; but in presence of a large excess of free acid, the action of the salt of ammonia will retain carbonate of baryta in solution, which, of course, will make the amount of sulphuric acid appear higher than is really the case. It need hardly be mentioned that this method is altogether inapplicable in presence of phosphoric acid, oxalic acid, or any other acid precipitating baryta salt from neutral solutions, and that no other bases but alkalies may be present.

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* Jahresber. von KOPP und WILL. 1861, 323, note.

† Compare my paper in Zeitschr. f. anal. Chem. 9, 52.

‡ Ann. der Chem. u. Pharm. 90, 165.

b. After A. Clemm.* Clemm has modified C. Mohr's process as follows with the view of making it more rapid in execution and more convenient for use in manufactories. In this also the absence is necessary of all other acids which form insoluble salts with baryta and of all bases except alkalies. We require besides the standard solutions mentioned in *a*, a normal solution of pure carbonate of soda, containing 53·04 grm. of the anhydrous salt in 1 litre. Put the solution of sulphuric acid into a measuring flask, add tincture of litmus, and if necessary neutralize exactly with soda free from carbonic acid or with hydrochloric acid, add a measured quantity of chloride of barium in excess, then a volume of carbonate of soda equal to that of the chloride of barium, fill to the mark, shake, filter and determine in an aliquot part of the filtrate (about a half) the carbonate of soda according to § 220. The acid used to neutralize the carbonate of soda left in the solution is equivalent to the sulphuric acid present. $KO,SO_3 + 2BaCl = BaO,SO_3 + KCl + BaCl$ and $BaO,SO_3 + KCl + BaCl + 2NaO,CO_2 = BaO,SO_3 + KCl + BaO,CO_2 + NaCl + NaO,CO_2$. In dilute solutions the small excess of carbonate of soda has no action on the sulphate of baryta, so that no error can arise on this score. The results are sufficiently accurate for technical purposes.

c. After E. Bohlig.† This method is intended for technical purposes. It depends on the fact that when an alkaline sulphate is heated at a temperature near 100° with precipitated carbonate of baryta in the presence of excess of carbonic acid complete decomposition takes place with formation of sulphate of baryta and alkaline bicarbonate. The amount of alkali combined with carbonic acid is determined alkalimetrically, it corresponds to the quantity of sulphuric acid. Regarding the details see the original paper.

d. After R. Wildenstein (First process‡). The principle of the method consists in precipitating the sulphuric acid with chloride of barium, and estimating the excess of the latter by means of neutral chromate of potassa; the chromate being added directly if the solution is neutral; if, on the contrary, it is acid, after addition of ammonia free from carbonic acid in slight excess. Two solutions are employed—

1. A solution of chloride of barium, 1 c.c. of which corresponds

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* Zeitschr. f. anal. Chem. 9, 122. † *Ib.* 9, 310. ‡ *Ib.* 1, 323.

to ·02 sulphuric acid. Prepared by dissolving 60·98 grm. of the pure crystallized salt to 1 litre.

2. A solution of pure neutral chromate of potassa, 2 c.c. of which precipitate 1 c.c. of the chloride of barium solution. Prepared by dissolving 18·45 grm. of bichromate of potassa, adding ammonia till the reddish-yellow color has turned to pale yellow, and diluting to 1 litre.

The first thing is to test whether the two solutions stand in the proper relation to one another. To this end take 10 c.c. of the chloride of barium solution, dilute with about 50 c.c. water, heat to boiling, and add 20·4 c.c. of the chromate of potassa solution. The precipitate soon settles, and the supernatant fluid must be yellowish. Add now chloride of barium drop by drop from the burette—·2 c.c. should be required.

For the actual analysis, dissolve the substance in about 50 c.c. water in a flask of, say 200 c.c., heat to boiling, and run in chloride of barium, till the whole of the sulphuric acid is certainly precipitated, but avoiding a large excess of the precipitant. Boil now for half to one minute, and if acid, neutralize with ammonia free from carbonic acid, and add, no matter whether the fluid is turbid or not, chromate of potassa in quantities of ·5 c.c. at a time. The fluid now rapidly becomes clear on gentle agitation, so that one can easily recognise, by the first appearance of the yellow coloration, when the chromic acid ceases to be precipitated. As soon as this point is reached, add chloride of barium slowly, drop by drop, till the fluid is again completely decolorized; for this purpose generally only a few drops, at the most only ·4 c.c., are required. Finally divide the c.c. of chromate used by 2, deduct them from the whole of the chloride of barium used, and reckon the sulphuric acid from the remainder. Results good.

In applying the method to sulphate of magnesia, zinc or cadmium, dissolve in ammonia with addition of chloride of ammonium, heat with a little chloride of calcium in order to throw down any carbonic acid in the ammonia, and then titrate (Fleischer*).

e. After R. Wildenstein (Second process†). Of all the methods for the volumetric estimation of sulphuric acid, the simplest and that which is capable of the most general application, is to drop into the solution containing excess of hydrochloric acid, standard chloride of barium solution, till the exact point is reached when no more precipitation takes place. This point is difficult to hit, and hence the method has only found a very limited use.

Wildenstein has given this method a practical form, which renders it possible to complete an analysis in about half an hour, and at the same time to obtain satisfactory results. He employs the apparatus, fig. 86. *A* is a bottle of white glass, whose bottom has been removed, it contains 900—950 c.c. *B* is a strong funnel-tube, with bell-shaped funnel, and bent as shown, provided below with a piece of india-rubber tube, a screw compression-cock, and a small piece of tubing not drawn out. The length

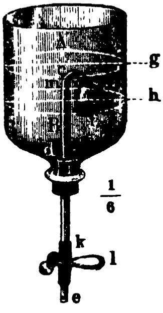

Fig. 86.

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* Journ. f. prakt. Chem. N F. 5, 318. Here also a modification of the process is suggested by which excess of chromate of ammonia may be detected in colored fluids, but this makes it rather complicated.

† Zeitschr. f. anal. Chem. 1, 432.

from *c* to *d* is about 7½-8, from *d* to *e* about 12 cm. The opening of the funnel-tube *f*, which should have a diameter of 2·5 to 3 cm., is covered as follows:—Take a piece of fine new calico or muslin, free from sulphuric acid, and about 6 cm. square, lay on it two pieces of Swedish paper of the same size, and then another piece of stuff like the first, now bind these altogether over the opening *f*, carefully and without injuring the paper, by means of a strong linen thread which has been drawn a few times over wax, and cut it off even all round. We have now a small syphon-filter, which enables us to filter off a portion of fluid contained in *A*, and turbid from sulphate of baryta, clear and with comparative rapidity.

On gradually adding chloride of barium to the dilute acid solution of a sulphate a point occurs which may be compared to the neutral point in precipitating silver with chloride of sodium (see p. 236); *i.e.*, there is a certain moment, when a portion filtered off will give a turbidity both with sulphuric acid and chloride of barium after the lapse of a few minutes. On this account we must either proceed on the principle recommended for the estimation of silver, *i.e.*, disregarding the quantity of chloride of barium in the solution, to standardize it by adding it to a known amount of sulphate, till a precipitate ceases to be formed; or else we must—and WILDENSTEIN recommends this latter course—consider as the end-point of the reaction the point at which chloride of barium ceases to produce a distinctly visible precipitation in the clear filtrate after a lapse of two minutes.

The chloride of barium solution is prepared as in *b*, so that 1 c.c. corresponds to ·02 sulphuric acid. The process is as follows:—

First prepare the solution of the sulphate to be analysed (using about 3 or 4 grm.), then fill *A* with hot water, open the cock with the screw or by the aid of a glass rod, and wait till the syphon *B* is quite full of water. If the water runs down the tube *c e* without filling it entirely, close and open the cock a few times, and this inconvenience will be removed. (It is not allowable to suck at *e*, or to fill the syphon with the wash-bottle at *e*, as either proceeding would inevitably lead to injuring the filter.) Now close the cock and pour out the hot water, replace it by 400 c.c. of boiling water, add the ready-prepared solution of the sulphate, and a small quantity of hydrochloric acid, if necessary, and run in the chloride of barium solution, at first in rather large portions, at last in ⅕ c.c. Before each fresh addition of chloride of barium open the cock and allow rather more liquid to flow into a beaker than corresponds to the contents of the syphon. This quantity should be previously ascertained, and a mark indicating it made on the beaker. Now close the cock and pour the filtrate without loss back into *A*. (As the beaker is used over and over again for the same purpose it need not be rinsed out.) Now run some of the fluid into a test tube, so as to one-third fill it, add to the clear fluid 2 drops of chloride of barium from the burette and shake. If a precipitate or turbidity is produced return the portion to the main quantity. The experiment is finished when the last portion tested shows after the lapse of exactly two minutes no distinctly visible turbidity. The drops of chloride of barium used for the last testing are of course not reckoned. The slight error involved from the fact that the small quantity of fluid in the syphon is finally unacted on, is too small to be noticed. During the experiment the filter must not be injured by the stirring. In case the end reaction has been overstepped, add 1 c.c. of dilute sulphuric acid (equivalent to the chloride of barium) to *A*, and endeavour to hit it again. Here 1 c.c. will have to be subtracted from the c.c. of chloride of barium used.

The results obtained by WILDENSTEIN are of sufficient accuracy for technical purposes. Some experiments made in my own laboratory were also quite satisfactory.

f. The methods of LEVOL,* PAPPENHEIM,† and SCHWARZ,‡ depend upon the precipitation of the sulphuric acid with standard solution of lead. Their use is limited, as they require the absence of chlorides, hydrochloric acid, and neutral ammonia salts.

II. SEPARATION OF SULPHURIC ACID FROM THE BASES.

a. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS SOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

The solution should be free from nitric acid. Precipitate the sulphuric acid according to I. by chloride of barium (or acetate of baryta). The filtrate contains the excess of chloride of barium, together with the chlorides of the bases present; determine the bases by the methods given in the fifth section for their separation from baryta. The fluid obtained by treating the ignited sulphate of baryta with hydrochloric acid, evaporating and filtering from the small amount of sulphate of baryta, must be added to the solution containing the bases. If after treating the sulphate of baryta with hydrochloric acid it still contains foreign bases, dissolve it in sulphuric acid with heat, pour the solution into cold water, and collect the precipitate on a filter; the remainder of the foreign base will then be found in the filtrate.

b. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS INSOLUBLE OR DIFFICULTLY SOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

a. From baryta, strontia, and lime: Fuse the finely pulverized substance, in a platinum crucible, with 5 parts of mixed carbonates of soda and potassa. Put the crucible, with its contents, into a beaker, or into a platinum or porcelain dish, pour water over it, and apply heat until the alkaline sulphates and carbonates are completely dissolved; filter the hot solution from the residuary carbonates of the earths, wash the latter thoroughly with water, to which a little ammonia and carbonate of ammonia has been added, and determine according to §§ 101 to 103. If the precipitates have been well washed, it is perfectly admissible to ignite and weigh at once. Precipitate the sulphuric acid from the filtrate, as in I. Finely pulverized sulphate of lime and sulphate of strontia may be completely decomposed also by boiling with a solution of carbonate of potassa;§ the same process will answer also for sulphate of baryta; but the operation is far more difficult, and complete decomposition is effected only by boiling the precipitate, after decanting the fluid, repeatedly with an excess of solution of carbonated alkali (H. ROSE‖).

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* Bulletin de la société d'Encour. Avril 1853; Journ. f. prakt. Chem. 60, 384.

† MOHR's Lehrb. der Titrirmethode, 3 Aufl. 411.

‡ Zeitschr. f. anal. Chem. 2, 392.

§ Carbonate of soda does not answer as well.

‖ Journ. f. prakt. Chem. 64, 382, and 65, 316.

β. *From oxide of lead:* The simplest way of effecting the decomposition of sulphate of lead consists in digesting it, at the common temperature, with a solution of bicarbonate of soda or potassa, filtering, washing the precipitate, determining the sulphuric acid in the filtrate as in I., dissolving the precipitate, which contains alkali, in nitric or acetic acid, and determining the lead in the solution, by one of the methods given in § 162.

Presence of strontia and lime necessitates no alteration in this method; but if baryta also is present, and it is accordingly necessary to ignite* the mixture with carbonated alkalies (or to boil repeatedly with fresh portions of solution of the same,) a small portion of lead always remains in solution in the alkaline fluid; this must be precipitated by passing carbonic acid before filtering.

γ. *From suboxide of mercury:* Sulphate of suboxide of mercury is best dissolved by warming with dilute hydrochloric acid with addition of chlorate of potassa or bromine, and the solution is treated according to *a*. If the salt is boiled with solution of carbonate of potash, the carbonate of suboxide of mercury first formed is decomposed, and the residue contains metallic mercury and oxide of mercury; a small part of the latter passes into the filtrate.

III. ESTIMATION OF FREE SULPHURIC ACID IN PRESENCE OF SULPHATES.

We have occasionally to estimate the free acid in presence of sulphates, as, for instance, in vinegar, wine, &c. This may be frequently done by indirect methods, the amount of the bases being determined on the one hand, and on the other the amount of the acids; sometimes also by determining the total quantity of sulphuric acid and the quantity of free acid, the latter by the acidimetric method. According to A. GIRARD† the following is the only direct method, which can be relied on. Evaporate on the water-bath to dryness and exhaust the residue with absolute alcohol; determine the combined acid in the residue, and the free acid in the alcoholic extract, after mixing with water and evaporating off the alcohol. It has been said that the object may be attained by the use of carbonate of baryta, which is supposed to throw down the free acid only, but this is erroneous since alkaline sulphates in aqueous solution are partially decomposed at the ordinary temperature by carbonate of baryta.

Supplement to the Second Division.

§ 133.

HYDROFLUOSILICIC ACID.

If you have hydrofluosilicic acid in solution, add solution of chloride of potassium, then a volume of strong alcohol equal to the fluid present, collect the precipitated silicofluoride of potassium on a weighed filter, and wash with a mixture of equal volumes of spirit of wine and water. Dry the washed precipitate at 100°, and weigh. Mix the alcoholic filtrate with hydrochloric acid, evaporate to dryness, and treat the residue with hydrochloric acid and water. If this leaves an undissolved residue of silicic acid, this is a sign that the examined acid contained an excess of silicic acid; the weight of the residue shows the amount of excess. Silicofluoride of potassium dried at 100° has the formula KF,SiF_2; for its properties, see § 68. Instead of weighing it, it may be estimated volumetrically according to § 97, 5. The analysis of metallic silicofluorides is best effected by heating in platinum vessels, with concentrated sulphuric acid; fluoride of silicon and hydrofluoric acid volatilize, the bases are left behind in the form of sulphates, and may, in many cases, after volatilization of the excess of sulphuric acid, be weighed as such. If the metallic silicofluorides to be analysed contain water, the latter cannot be estimated by mere ignition, since fluoride of silicon would escape with the water. H. ROSE recommends the following method: Mix them most intimately with 6 parts of recently ignited oxide of lead, cover the mixture, in a small retort, with a layer of pure oxide of lead, weigh the retort, heat cautiously until the contents begin to fuse together, remove the aqueous vapor still remaining in the vessel by suction, and weigh the retort again when cold. The diminution of weight shows the quantity of water expelled. Do not neglect testing the drops of the escaping water with litmus paper; the result is accurate only if they have no acid reaction.

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* This is best done in a porcelain crucible.

† Compt. rend. 58, 515; Zeitschr. f. anal. Chem. 4, 219.

F. STOLBA* proposes the following process, at least for compounds soluble in water. Put into a crucible double as much magnesia as is necessary to decompose the silicofluoride to be analysed, ignite it as strongly as possible, allow to cool, and weigh. Add water to form a thick paste, and then the weighed silicofluoride; if the amount of water present is not enough to dissolve the compound, add some more, mix with a platinum wire which must afterwards be wiped off clean, dry, ignite, and weigh. The increase in weight shows the amount of anhydrous silicofluoride, provided no oxide is present which takes up oxygen.

Third Division of the First Group of the Acids.

PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID.

§ 134.

1. PHOSPHORIC ACID.

I. DETERMINATION.

Tribasic phosphoric acid may be determined in a great variety of ways. The forms in which this determination may be effected have been given already in § 93, 4. The most appropriate forms for the purpose, however, are *pyrophosphate of magnesia* and *phosphate of sesquioxide of uranium*, because they are in themselves well worthy of recommendation and can be employed in almost all cases. The determination as pyrophosphate of magnesia is frequently preceded by precipitation in another way, especially as phospho-molybdate of ammonia, occasionally as phosphate of binoxide of tin or of suboxide of mercury. The other forms in which phosphoric acid may be determined give also, in part, very good results, but admit only of a more limited application. With respect to volumetric methods, those which depend upon the use of standard solution of uranium are the best.

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* Zeitschr. f. anal. Chem. 7, 93.

With regard to meta- and pyrophosphoric acids, I have simply to remark here that these acids cannot be determined by any of the methods given below. The best way to effect their determination is to convert them into tribasic phosphoric acid; as follows:—

α. In the dry way. By protracted fusion with from 4 to 6 parts of mixed carbonates of soda and potassa. This method is, however, applicable only in the case of meta- and pyrophosphates of the alkalies, and of those meta- or pyrophosphates of metallic oxides which are completely decomposed by fusion with alkaline carbonates; it fails, accordingly, for instance, with the salts of alkaline earths, magnesia excepted.

β. In the wet way. The salt is heated for some time with a strong acid, best with concentrated sulphuric acid (WEBER[*]). This method leads only to the attainment of approximate results, in the case of all salts whose bases form soluble compounds with the acid added, since in these cases the meta- or pyrophosphoric acid is never completely liberated; but the desired result may be fully attained by the use of any acid which forms insoluble compounds with the bases present. Respecting the partial conversion in the former case, I have found that it approaches the nearer to completeness the greater the quantity of free acid added,[†] and that the ebullition must be long continued (comp. Expt. No. 32).

BUNCE's statement,[‡] that phosphoric acid volatilizes when a phosphate is evaporated to dryness with hydrochloric or nitric acid and the residue heated a little, is quite erroneous (compare my paper on the subject, in Annal. der Chem. und Pharm, 86, 216). But, on the other hand, it must be borne in mind that tribasic phosphoric acid under these circumstances changes, not indeed at 100°, but at a temperature still below 150°, to pyrophosphoric acid; thus, for instance, upon evaporating common phosphate of soda with hydrochloric acid in excess, and drying the residue at 150°, we obtain $NaCl + NaO,HO,PO_5$.

a. Determination as Phosphate of Lead.

Proceed as with arsenic acid, § 127, 1, *a*—*i.e.*, evaporate with a weighed quantity of oxide of lead, and ignite. This method presupposes that no other acid is present in the aqueous or nitric acid solution; it has this great advantage that it gives correct results, no matter whether the phosphoric acid present is mono-, bi-, or tribasic.

b. Determination as Pyrophosphate of Magnesia.

α. Direct determination. Suitable in all cases in which it is quite certain that the acid is present in the tribasic state, either free or combined with an alkali.

The solution should be neutral or only moderately ammoniacal. Add chloride of ammonium, and then the usual magnesia mixture (§ 62, 6), or, still better, a mixture of chloride of magnesium, chloride of ammonium and ammonia,[*] in sufficient but not too excessive quantity. 10 c.c. of the magnesia mixture will precipitate ·24 grm. PO_5. The precipitate being under these conditions somewhat slowly formed, appears distinctly crystalline. After some time add ammonia gradually to the amount of one-third of the fluid. Allow to stand 12 hours in a well-covered vessel in the cold, filter, test the filtrate with magnesia mixture and ammonia, and wash the precipitate with ammonia diluted with 3 volumes of water till the washings, when acidified with nitric acid and tested with nitrate of silver, are no longer rendered turbid; proceed according to § 104, 2. The precipitate is not absolutely insoluble in ammoniated water, therefore it is well to wash by suction, as this reduces the necessary amount of wash water to a minimum. The results are accurate (Expt. No. 80, also Kissel).[†] If there is reason to suspect the purity of the precipitate, dissolve it in hydrochloric acid, and throw down again with ammonia, adding some magnesia mixture. If the magnesia mixture is omitted, the solution being free from magnesia, will dissolve some of the precipitate. Compare Kissel, *loc. cit.* Properties of the precipitate and residue § 74. If the solution contains pyrophosphoric acid, the precipitate is flocculent and dissolves to a notable degree in ammoniated water (Weber).

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[*] Pogg. Annal. 73, 137.

[†] There are, however, other considerations which forbid going too far in this respect.

[‡] Sillim. Journ. May, 1851. 405.

β. *Indirect determination*, with previous precipitation as ***phosphomolybdate of ammonia***, after Sonnenschein.[‡]

Applicable in all cases in which the phosphoric acid is present in the tribasic state, even in presence of alkaline earths, alumina, sesquioxide of iron, &c. Tartaric acid, however, and similarly acting organic substances must be absent. No considerable quantity of hydrochloric acid may be present. Large quantities of chloride of ammonium, and of metallic chlorides generally, also of certain ammonia salts, especially the oxalate and citrate (König)[§], are to be avoided. Nitrate of ammonia assists the precipitation and neutralizes the injurious action of very large quantities of nitrates and sulphates (E. Richters)[‖]. The molybdenum solution described "Qual. Anal.," § 52, is employed as the precipitant. It contains 5 per cent. of molybdic acid. The fluid to be examined for phosphoric acid should be concentrated, it may contain free nitric or free sulphuric acid. Transfer to a beaker and add a considerable quantity of the molybdenum solution. About 40 parts molybdic acid must be added for every 1 part phosphoric acid, therefore 80 c.c. of the molybdic solution for ·1 grm. phosphoric acid. Stir, without touching the sides, and keep covered 12 hours at about 40°. Then remove a portion of the clear supernatant fluid with a pipette, mix it with an equal volume of molybdenum solution, and allow it to stand some time at 40°. If a further precipitation takes place, return the portion to the main quantity, add more molybdenum solution, allow to stand again 12 hours, and test again. When complete precipitation has been effected pour the fluid off through a small filter and wash the precipitate entirely by decantation, using a mixture of 100 parts molybdate solution, 20 parts nitric acid of 1·2 sp. gr., and 80 parts water.[*] The washing must be thorough, and the last runnings must not be precipitated by excess of ammonia, even if lime, iron, &c., was present in the solution. Now dissolve the precipitate in the least quantity of ammonia, pour the fluid through the small filter, when the minute amount of precipitate thereon will be dissolved, wash the filter with ammonia diluted with three volumes of water, mix the filtrate and washings, and add hydrochloric acid carefully till the precipitate produced, instead of redissolving instantly, takes a little time to disappear; finally throw down with magnesia mixture (compare *a*). If the ammonia leaves a small amount of the precipitate undissolved, treat the residue with nitric acid and test the filtrate with molybdic solution in order to save any phosphoric acid. Results accurate.[†]

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[*] When the ordinary mixture is used a little deviation from the correct process may cause the precipitate to contain a trace of basic sulphate of magnesia. The mixture recommended is prepared as follows:—Dissolve 83 grm. crystallized sulphate of magnesia in boiling water, add 5 c.c. hydrochloric acid, then 82 grm. crystallized chloride of barium dissolved in water, boil, decant, filter, and test whether dilute sulphuric acid gives any precipitate in the filtrate; if it does add a little more sulphate of magnesia. Mix the filtrate and washings, concentrate by evaporation, allow to cool, transfer to a litre flask, add 165 grm. pure chloride of ammonium, 260 c.c. ammonia and water to the mark. Allow to stand a few days and filter if necessary. This solution contains the same quantity of magnesia as that given in § 62, 6.

[†] Zeitschr. f. anal. Chem. 8, 170. [‡] Journ. f. prakt Chem. 53, 343.

[§] Zeitschr. f. anal. Chem. 10, 305. [‖] *Ib.* 10, 469.

As this method requires so large a quantity of molybdic acid, it is usually resorted to only in cases where methods *b*, *a*, and *c* are inapplicable; and the phosphoric acid in the quantity of substance taken is not allowed to exceed ·3 grm. Arsenic acid and silicic acid,[‡] if present, must first be removed. Of all the methods for determining phosphoric acid which are admissible in the presence of sesquioxide of iron and alumina, this is the best in my opinion, especially for the estimation of small quantities of the acid in presence of large quantities of these bases.

γ. *Indirect determination*, with previous precipitation as *phosphate of suboxide of mercury*, after H. Rose.[§]

Applicable for the separation of phosphoric acid (also of pyro- and metaphosphoric acid) from all bases, except alumina. Comp. § 135, *k*.

Dissolve the phosphate in neither too large nor too small a quantity of nitric acid, in a porcelain dish, add pure metallic mercury in sufficient quantity to leave a portion, even though only a small one, undissolved by the free acid. Evaporate on the water-bath to dryness. If the warm mass still evolves an odor of nitric acid, moisten it with water, and heat again on the water-bath, until it smells no longer of nitric acid. Add now hot water, pass through a small filter, and wash until the washings leave no longer a fixed residue upon platinum. Dry the filter, which, besides the phosphate, contains also basic nitrate of suboxide of mercury and free mercury, mix its contents, in a platinum crucible, with mixed carbonates of soda and potassa in excess, roll the filter into the shape of a ball, place it in a hollow made in the mixture, and cover the whole with a layer of the mixed carbonates. Expose the crucible, under a chimney with good draught, for about half an hour to a moderate heat, so that it does not get red-hot. At this temperature, the nitrate of suboxide of mercury and the metallic mercury volatilize. Heat now over the lamp to bright redness, and treat the residue with hot water, which will dissolve it completely, if no sesquioxide of iron be present, and if no oxide of platinum has been formed. The latter may occur on account of too rapid heating, which might produce nitrate of soda, which would act upon the platinum. Supersaturate the clear (if necessary, filtered) solution with hydrochloric acid, add ammonia and magnesia-mixture, and proceed as in *a*.

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[*] According to E. Richters (Zeitschr. f. anal Chem. 10, 471) you may also wash with a solution of nitrate of ammonia containing 15 grm. in 100 c.c. slightly acidified with nitric acid and containing a few per-cents of molybdic acid solution.

[†] Zeitschr. f. anal. Chem. 3, 446, and 6, 403.

[‡] Silicic acid may also be thrown down, in form of a yellow precipitate, by acid solution of molybdate of ammonia, especially in presence of much chloride of ammonium (W Knop, Chem. Centralb. 1857, 691). Mr. Grundmann, who repeated Knop's experiments in my laboratory, obtained the same results. The precipitate dissolves in ammonia. If the solution, after addition of some chloride of ammonium, is allowed to stand for some time, the silicic acid separates, and the phosphoric acid may then be precipitated from the filtrate with magnesia-mixture; it is, however, always the safer way to remove silicic acid first

[§] Pogg. Annal. 76, 218.

δ. *Indirect determination*, with previous precipitation as *phosphate of binoxide of tin.*

aa. After W. Reissig.* The substance should be free from chlorides. Dissolve in concentrated nitric acid, add, at least, eight times as much of the purest tin (in the form of foil or small grains) as there is phosphoric acid present, and warm for five or six hours, until the precipitate has completely subsided.† Wash by decantation combined with filtration, rinse into a platinum dish, and digest with a small quantity of concentrated solution of potassa. The product of this operation is a mixture of metastannate and phosphate of potassa, which, upon addition of hot water, dissolves to a clear fluid, and even very readily if there has not been too much hydrate of potassa used. Dissolve, in the same way, the trifling particles of the precipitate which may still adhere to the filter, add this solution to that of the precipitate, transfer the whole fluid to a weighed flask of a litre capacity, and dilute with water to make the fluid up to about 900 grm.; saturate now with sulphuretted hydrogen, adding also some pentasulphide of ammonium, and then acetic acid, until the bisulphide of tin is precipitated, and the fluid *slightly* acid. Replace the flask now on the scale, add water, until the contents weigh 1000 grm. (or some other round number), shake, allow it to stand from 12 to 16 hours, filter the supernatant clear fluid into a porcelain dish, and weigh the flask again, which now contains the rest of the fluid, together with the sulphide of tin. The weight found gives, by simple subtraction, also the quantity of the filtrate in which the phosphoric acid is to be estimated. The proportion which this bears to the total quantity of the fluid, viz., 1000 grm. minus the weight of the sulphide of tin (which may be calculated with sufficient accuracy from the amount of tin originally used, or may be estimated in the direct way), is easily found.

Wash the filter used in transferring the clear fluid from the flask to the porcelain dish, and add the washings to the filtrate in the latter; evaporate the fluid to a small bulk, and estimate the phosphoric acid in this according to *b*, *a*. The way here recommended of effecting the separation of the phosphoric acid fluid from the sulphide of tin must be resorted to of necessity, since in the filtration and washing of the sulphide, no matter whether with pure water or water containing sulphuretted hydrogen, a small quantity of tin would inevitably be dissolved. Results accurate.

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* Annal. d. Chem. u. Pharm. 98, 339. The method is a judicious modification of Reynoso's process (Journ. f. prakt. Chem. 54, 261), which latter, though in principle free from defects, yet presents certain practical difficulties, owing principally to the large proportion of tin required for the process (eight times the quantity of the phosphoric acid), which makes the presence of even slight impurities in the tin a source of considerable error. These remarks of Reissig completely coincide with the results of my own experiments.

† In the presence of alumina or sesquioxide of iron portions of these bases pass into the precipitate (Girard).

bb. After Girard.* In order to render the method depending on the original separation of the phosphoric acid as phosphate of binoxide of tin, applicable in the presence of alumina and sesquioxide of iron, Girard proceeds as follows: having obtained the precipitate as in *aa*, consisting of metastannic acid and phosphate of binoxide of tin, together with a little phosphate of sesquioxide of iron and of alumina, and having washed it first by decantation, then on a filter, he heats it either at first with a small quantity of aqua regia, and then with ammonia and sulphide of ammonium, or immediately with sulphide of ammonium in excess. The last process is recommended by O. Baber,† on the ground that the former leaves a little phosphoric acid in the precipitate. The whole is digested about two hours, and then filtered; the precipitate, consisting of sulphide of iron and hydrate of alumina, is washed with warm sulphide of ammonium, then with water containing a little sulphide of ammonium, dissolved in nitric acid, and the solution thus formed mixed with the filtrate from the tin precipitate which contains the principal quantity of the bases. From the sulphide of ammonium filtrate, which contains bisulphide of tin and phosphate of ammonia, the phosphoric acid is at once precipitated by magnesia-mixture. I may add that Girard considers 4 to 5 parts tin sufficient for 1 part phosphoric acid. The results afforded by his test-analyses are unexceptionable. According to Janovsky,‡ at least six parts of tin must be used. If the tin contains arsenic the sulphide of ammonium solution should be treated according to *aa*, as direct precipitation with magnesia mixture would throw down a little arsenate of magnesia and ammonia with the phosphate.

ε. *Indirect determination*, with previous precipitation as *phosphate of bismuth*.

This method was proposed by Chancel,§ and modified by Birnbaum and Chojnaki.‖ It is not applicable in presence of sulphuric or hydrochloric acid and cannot lay claim either to quickness or accuracy.¶

c. Determination as Phosphate of Sesquioxide of Uranium.

After Leconte, A. Arendt, and W. Knop.** (Very suitable in presence of alkalies and alkaline earths, but not in presence of any notable amount of alumina; in presence of sesquioxide of iron, the method can be applied only with certain modifications).* Where it is possible, prepare an acetic acid solution of the salt. If you have a nitric or hydrochloric acid solution, remove the greater portion of the free acid by evaporation, add ammonia until red litmus paper dipped into it turns very distinctly blue, and then redissolve the precipitate formed in acetic acid. If mineral acids were present, add also some acetate of ammonia; this addition is beneficial under any circumstances. Mix the fluid now with solution of acetate of sesquioxide of uranium, and heat the mixture to boiling, which will cause the phosphoric acid to separate, in form of pale greenish-yellow phosphate of sesquioxide of uranium and ammonia.

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* Compt. rend. 54, 468; Zeitschrift f. analyt. Chem. 1, 366.

† Zeitschr. f. die gesammten Naturwissensch. 1864, 293.

‡ Zeitschr. f. anal. Chem. 11, 157.

§ Compt. rend. 50, 416; Chem. Centralbl. 1860, 272; Compt. rend. 51, 882; Chem. Centralb. 1861, 221.

‖ Zeitschr. f. anal. Chem. 9, 203.

¶ Compare Holzberger, Archiv der Pharm. (2) 116, 37; Baber, Zeitschr. f. die ges. Naturwiss. 1864, 293; Girard, Compt. rend. 54, 468; Fresenius, Neubauer, and Luck, Zeitschr. f. anal. Chem. 10, 135; Adriaansz, *ibid.* 10, 473.

** Leconte was the first to recommend the method of precipitating phosphoric acid from acetic acid solutions by means of a salt of uranium (Jahresb. von Liebig und Kopp, für 1853, 642); A. Arendt and W. Knop have subsequently subjected it to a careful and searching examination (Chem. Centralbl. 1856, 769, 803; and 1857, 177).

Wash the precipitate, first by decantation, boiling up each time, then by filtration; the operation may be materially facilitated by adding a few per-cents of nitrate of ammonia to the water. Dry the precipitate, and ignite as directed § 53. It is advisable to evaporate small quantities of nitric acid on the ignited precipitate repeatedly, and to re-ignite. The residue must have the color of the yolk of an egg. For the properties of the precipitate and residue, see § 93, 4, *e*. Should it be necessary to dissolve the ignited residue again, for the purpose of reprecipitating it, this can be done only after fusing it with a large excess of mixed carbonates of soda and potassa, and thereby converting the pyrophosphoric into tribasic phosphoric acid. Results accurate; compare the test-analyses given by the authors, Expt. No. 81, and KISSEL's experiments.†

d. Determination as Basic Phosphate of Sesquioxide of Iron.

a. Mix the acid fluid containing the phosphoric acid with an excess of solution of sesquichloride of iron of known strength, add, if necessary, sufficient ammonia to neutralize the greater portion of the free acid, mix with acetate of ammonia in not too large excess, and boil. If the quantity of solution of sesquichloride of iron added was sufficient, the precipitate must be brownish-red. This precipitate consists of basic phosphate and basic acetate of sesquioxide of iron, and contains the whole of the phosphoric acid and of the sesquioxide of iron. Filter off boiling, wash with boiling water mixed with some acetate of ammonia, dry carefully, and ignite in a platinum crucible with access of air (§ 53). Moisten the residue left upon ignition with strong nitric acid, evaporate this at a gentle heat, and ignite again. Should this operation have increased the weight, which, however, is not usually the case, it must be repeated, until the weight remains constant. Deduct from the weight of the residue that of the sesquioxide of iron contained in the solution added; the difference is the phosphoric acid.

[This modification of SCHULZE's method was first recommended by A. MÜLLER;‡ it has been adopted also by WAY and OGSTON, in their analyses of ashes.§ MÜLLER's improvement consists in the use of a solution of sesquichloride of iron of known strength, whereby the estimation of the sesquioxide of iron in the residue (which would have to be effected in the manner described § 113, 3) is dispensed with.]

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* Chem. Centralbl. 1857, 182. † Zeitschr. f. anal Chem. 8, 167.

‡ Journ. f. prakt. Chem. 47, 341.

§ Journal of the Royal Agricultural Society, viii. part i.

β. J. **WEEREN's** method, suitable for the estimation of the phosphoric acid in phosphates of the alkalies and alkaline earths.* Mix the nitric acid solution of the phosphate under examination, which must contain no other strong acid, with a solution of nitrate of sesquioxide of iron of known strength, in sufficient proportion to insure the formation of a basic salt (3 or 4 parts of sesquioxide of iron should be added for 1 part of phosphoric acid); evaporate to dryness, heat the residue to 160°, until no more nitric acid fumes escape, treat with hot water containing nitrate of ammonia until all nitrates of the alkalies and alkaline earths are removed, collect the yellow-ochreous precipitate on a filter, dry, ignite (see § 53), weigh, and deduct from the weight the quantity of sesquioxide of iron added. **LATSCHINOW**† recommends heating the residue to 200°, warming with water and a few drops of sulphuric acid, adding ammonia and then treating with hot solution of nitrate of ammonia. He says that the phosphoric acid is thus more completely separated, and the precipitate may be more readily filtered off.

e. Determination as Basic Phosphate of Magnesia ($3MgO,PO_5$).

(**FR. SCHULZE's** method, suitable more particularly to effect the separation of phosphoric acid from the alkalies.‡)

Mix the solution of the alkaline phosphate, which contains chloride of ammonium, with a weighed excess of pure magnesia, evaporate to dryness, ignite the residue until the chloride of ammonium is expelled, and separate the magnesia, which is still present in form of chloride of magnesium, by means of oxide of mercury (§ 104, 3, *b*). Treat the ignited residue with water, filter the solution of the chlorides of the alkali metals, wash the precipitate, dry, ignite, and weigh. The excess of weight over that of the magnesia used shows the quantity of the phosphoric acid. Results satisfactory.

f. **SCHLÖSING's** method§ does not appear to offer any advantages. The phosphate is mixed with silica and ignited in carbonic oxide, the expelled phosphorus being taken up by copper or nitrate of silver.

g. Determination by Volumetric Analysis (With Uranium Solution).

This method was recommended originally by **LECONTE**.‖ It was improved and described in detail by **NEUBAUER**,¶ and was afterwards recommended by **PINCUS**,** and subsequently by **BÖDEKER**.†† The *principle* of the method is as follows: acetate of sesquioxide of uranium precipitates from solutions rendered acid by acetic acid, phosphate of sesquioxide of uranium, or—in the presence of considerable quantities of ammoniacal salts—phosphate of sesquioxide of uranium and ammonia. The proportion between the uranium and the phosphoric acid is the same in both compounds. Both compounds when freshly precipitated and suspended in water are left unchanged by ferrocyanide of potassium; acetate of sesquioxide of uranium, on the other hand, is indicated by this reagent with great delicacy, insoluble reddish-brown ferrocyanide of uranium being precipitated.

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* Journ. f. prakt. Chem. 67, 8. † Zeitschr. f. anal. Chem. 7, 213.

‡ Journ f. prakt. Chem. 63, 440.

§ Zeitschr. f. anal. Chem. 4, 118, and 7, 473.

‖ Jahresber. von LIEBIG u. KOPP, für 1853, 642.

¶ Archiv für wissenschaftliche Heilkunde, 4, 228.

** Journ. f. prakt. Chem. 76, 104.

†† Annal. d. Chem. u. Pharm. 117, 195.

According to **Neubauer*** the following *solutions* are employed :—

a. A solution of phosphoric acid of known strength. Prepared by dissolving 10·085 grm. pure, crystallized, uneffloresced, powdered, and pressed phosphate of soda in water to 1 litre. 50 c.c. contain ·1 grm. PO_5. It is well to control this solution by evaporating 50 c.c. in a weighed platinum dish to dryness, igniting strongly, and weighing. The weight should be ·1874 grm.

b. An acid solution of acetate of soda. Prepared by dissolving 100 grm. acetate of soda in 900 water, and adding acetic acid of 1·04 sp. gr. to 1 litre.

c. A solution of acetate (or nitrate) of sesquioxide of uranium (§ 63, 3). This is standardized by means of the phosphate of soda solution. 1 c c. indicates ·005 grm. PO_5. The solution is made at first a little stronger than necessary, so that it may contain in the litre say 22 grm. Ur_2O_3 (corresponding to 32·5 grm. $Ur_2O_3,\bar{A} + 2$ aq. or 34 grm. $Ur_2O_3,A + 3$ aq.), its value is determined, and it is diluted accordingly. To determine its value proceed as follows: transfer 50 c.c. of the *a* solution to a beaker, add 5 c.c. of the *b* solution, and heat in a water-bath to 90—100°. Now run in uranium solution, at first a large quantity, at last in ½ c.c., testing after each addition whether the precipitation is finished or not. For this purpose spread out one or two drops of the mixture on a white porcelain surface and introduce into the middle, by means of a thin glass rod, a small drop of freshly prepared ferrocyanide of potassium solution or a little of the powdered salt. As soon as a trace of excess of acetate of uranium is present, a reddish-brown spot forms in the drop, which, surrounded as it is by the colorless or almost colorless fluid, may be very distinctly perceived. When the final reaction has just appeared, heat a few minutes in the water bath and repeat the testing on the porcelain. If now the reaction is still plain the experiment is concluded. If the uranium solution had been exactly of the required strength, 20 c.c. would have been used; but it is actually too concentrated, hence less than 20 c.c. must have been used. Suppose it was 18 c.c., then the solution will be right, if for every 18 c.c. we add 2 c.c. of water. If in this first experiment we find that the solution is much too strong, the solution is diluted with somewhat less water than is properly speaking required, another experiment is made, and it is then diluted exactly.

The *actual analysis* must be made under as nearly as possible similar circumstances to those under which the standardizing of the uranium solution was performed, especially as regards the acetate of soda. This salt retards the precipitation of uranium by ferrocyanide of potassium, hence the test drop on the porcelain plate becomes darker and darker. The analyst should accustom himself to observing the first appearance of the slightest brownish coloration in the middle of the drop, and should take this as the end-reaction. It need hardly be added that the same person must make the analysis who has standardized the solution (**Neubauer**).

The method is applicable to free phosphoric acid, alkaline phosphates, and phosphate of magnesia, also in the presence of small quantities of the phosphates of other alkaline earths, but cannot be employed in presence of sesquioxide of iron and alumina. Dissolve the substance in water or the least possible quantity of acetic acid, add 5 c.c. of the *b* solution, dilute to 50 c.c., and proceed with the addition of uranium as above. The results are very satisfactory. Compare KISSEL's experiments.* If the above process is followed in the presence of much lime, for instance with a solution of basic phosphate of lime in dilute acetic acid, the results are almost always too low, as a little phosphate of lime is liable to separate when the fluid is heated. This difficulty may be easily obviated by adding the phosphate solution to the uranium, till ferrocyanide of potassium ceases to give a reaction (R. FRESENIUS, NEUBAUER, and LUCK)†. The operation of standardizing the uranium will then take the following form.

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* His Anleitung zur Harnanalyse, 6 Aufl. 171.

Transfer 25 c.c. of the uranium solution to a beaker, add 5 c.c. of the acetate of soda and 3 c.c. acetic acid of 1·04 sp. gr., heat in the water-bath and run in the standard phosphate of soda from a burette, till a drop taken out just ceases to give a reaction with a little powdered ferrocyanide of potassium on a porcelain plate. After each fresh addition of phosphate, replace the beaker in the boiling water and wait a few minutes before testing. Of course the phosphate may be added without fear as long as the fluid remains yellowish. In making the analysis take care that the lime solution does not contain too large an excess of acetic acid, that its state of concentration does not differ greatly from that of the standard phosphate of soda, and that its total quantity is known before the burette is filled.

There are other volumetric methods proposed by FLEISCHER‡ (with alumina), and SCHWARZ§ (with lead). The latter depends on a correct principle, and is sufficiently exact for neutral fluids; but, the presence of acetic acid being injurious, its use is extremely limited. See FR. MOHR.‖

II. SEPARATION OF PHOSPHORIC ACID FROM THE BASES.

a. From the Alkalies (see also *d, k, u, l*).

α. Add chloride of ammonium, or hydrochloric acid, then acetate of lead, exactly, till no more precipitate is produced, and lastly some pure carbonate of lead (prepared by precipitating acetate of lead with carbonate of ammonia, BÄBER¶), allow to digest for some time, filter off the precipitate consisting of phosphate, chloride, and carbonate of lead, wash, precipitate from the filtrate the slight excess of lead by sulphuretted hydrogen, filter and evaporate with hydrochloric acid (in the case of lithia, sulphuric acid). If the phosphoric acid is to be estimated in the same portion, proceed with the first precipitate (after washing to remove the larger quantity of chloride), according to *b*.

β. (Only applicable in the case of fixed alkalies). Separate the phosphoric acid as phosphate of sesquioxide of iron, according to one of the methods given § 134, *d*. Or if you do not wish to estimate the phosphoric acid it is very convenient to acidify with hydrochloric acid, add sesquichloride of iron, dilute rather considerably, add ammonia till the fluid is neutral, and boil; all the phosphoric acid will then separate with the basic sesquichloride of iron as phosphate of iron. The separation of phosphoric acid may also be effected as basic phosphate of magnesia (§ 134, *e*). The alkalies are contained in the filtrate as nitrates or chlorides.

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* Zeitschr. f. anal. Chem. 8, 167. † *Ib.* 10, 147.

‡ *Ib.* 4, 19 and 6, 28.

§ Dingler's polyt. Journ. 169, 289; Zeitschr. f. anal. Chem. 2, 392.

‖ Zeitschr. f. anal. Chem. 2, 256.

¶ Zeitschr. f. die ges. Naturwiss. 1864, 298; Zeitschr. f. anal. Chem. 4, 120.

b. From Baryta, Strontia, Lime, and Oxide of Lead.

The compound under examination is dissolved in hydrochloric or nitric acid, and the solution precipitated with sulphuric acid in slight excess. In the separation of phosphoric acid from strontia, lime, and oxide of lead, alcohol is added with the sulphuric acid. The phosphoric acid in the filtrate is determined according to § 134, *b*, *a*, after removal of the alcohol by evaporation. The determination of the phosphoric acid is effected most accurately by saturating the fluid with carbonate of soda, evaporating to dryness, and fusing the residue with the carbonates of soda and potassa. The fused mass is then dissolved in water, and the further process conducted as in § 134, *b*, *a*.

c. From Magnesia (see also *d*, *h*, *k*, *l*).

Add sesquichloride of iron in sufficient excess, dilute, add excess of carbonate of baryta, allow to remain for several hours with frequent stirring, filter and separate magnesia and baryta in the filtrate after § 154.

d. From the whole of the Alkaline Earths and fixed Alkalies (comp. *h*, *k*, *l*).

a. Dissolve in the least possible quantity of nitric acid, add a little chloride of ammonium, precipitate exactly with acetate of lead, add a little carbonate of lead (precipitated), digest, filter, precipitate the excess of lead rapidly from the filtrate by sulphuretted hydrogen, filter and determine the bases in the filtrate. Results good.

β. Dissolve in water, and—in the case of alkaline earthy phosphates—the least possible nitric acid, add neutral nitrate of silver and then carbonate of silver, till the fluid reacts neutral. All phosphoric acid now separates as $3AgO,PO_5$. Warming is unnecessary. Filter, wash the precipitate, dissolve it in dilute nitric acid, precipitate the silver with hydrochloric acid, and determine the phosphoric acid in the filtrate according to § 134, *b*, *a*. The filtrate from the phosphate of silver is freed from silver by hydrochloric acid, and the bases are then determined according to the methods already given (G. CHANCEL*). A good and convenient method unless the proportion of alkali is very large. (If the substance contains alumina or sesquioxide of iron, these bases are completely precipitated by the carbonate of silver, and are found mixed with the phosphate of silver.)

γ. Separate the phosphoric acid as phosphate of sesquioxide of uranium (§ 134, *c*), and the excess of sesquioxide of uranium from the alkaline earths, &c. in the filtrate, according to §§ 160 and 161, Supplement. Results good.

δ. Separate the phosphoric acid according to § 134, *d*, *a* or *β*. The alkaline earths are obtained in solution in the first case, as chlorides, together with alkaline acetate and chloride; in the second case as nitrates. Results good.

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* Compt. rend. 49, 997.

e. From Alumina.

The best method of separating phosphoric acid from alumina is that depending on precipitation by molybdate of ammonia (*l*). The separation of the acid as phosphate of binoxide of tin (*h*, *a*) is also satisfactory. The older methods are now scarcely ever employed, and I will therefore only briefly describe the two which were formerly most in use.

a. OTTO's method. The fluid is mixed with tartaric acid and ammonia, and the phosphoric acid is precipitated with magnesia-mixture. It is very difficult, even by repeated precipitation, to obtain a precipitate free from alumina. On the other hand, a small part of the phosphoric acid remains in solution. Compare ILYREN,* F. KNAPP,† and R. PRIBRAM.‡

β. After BERZELIUS. Pulverize the compound very finely, mix with about 1½ parts of pure silicic acid§ and 6 parts of carbonate of soda, in a platinum crucible, and expose for half an hour to a strong red heat. Macerate the ignited mass in water, add bicarbonate of ammonia in excess, digest for some time, then filter and wash. On the filter you have now silicate of alumina and soda, in the solution phosphate of soda, bicarbonate of soda, and carbonate of ammonia. (Were the solution filtered before the addition of the bicarbonate of ammonia, it would contain also some of the alumina.) Determine the phosphoric acid in the solution as directed in § 134, *b*, *a*, and separate and determine the alumina in the insoluble residue in the manner described § 140. The method is troublesome and tedious, the precipitate being difficult to wash; but the results are accurate. Compare SCHWEITZER.‖

f. From Sesquioxide of Chromium (see also *h*, *k*, *l*).

Fuse with carbonate and nitrate of soda, and separate the chromic acid and phosphoric acid in the manner described § 166.

g. From the Metallic Oxides of the Fourth Group (see also *h*, *k*, *l*).

a. The method so often used of fusing with carbonate of soda does not give accurate results on account of the constant presence of some phosphoric acid in the washed residue. Compare W. SCHWEIKERT¶ and G. SCHWEITZER.** The former has studied the separation of oxide of zinc from phosphoric acid by this method, the latter the separation of sesquioxide of iron.

β. Dissolve in hydrochloric acid, add tartaric acid, chloride of ammonium and ammonia, and finally, in a flask which is to be closed afterwards, sulphide of ammonium, put the flask in a moderately warm place, allowing the mixture to deposit until the fluid appears of a yellow color, without the least tint of green; filter, and determine the metals as directed in §§ 108 to 114. The phosphoric acid is found from the loss or determined according to § 134, *b*, *a*. The magnesia-mixture may immediately be added to the filtrate, which contains sulphide of ammonium. The washed precipitate is redissolved in just sufficient hydrochloric acid, and the solution reprecipitated by ammonia with addition of magnesia-mixture. This method is not well adapted for phosphate of nickel.

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* Journ. de Pharm. 21, 28. † Zeitschr. f. anal Chem. 4, 151.

‡ Vierteljahresschr. f. prakt. Pharm. 15, 184.

§ The safest way is to use artificially prepared silicic acid.

‖ Zeitschr. f. anal Chem. 9, 89.

¶ Annal. d. Chem. u. Pharm. 145, 57 ; Zeitschr. f. anal. Chem. 7, 246.

** Zeitschr. f. anal. Chem. 9, 84.

h. From Metallic Oxides of the Second, Third, and Fourth Groups.

α. More especially from the alkaline earths, alumina, the oxides of manganese, nickel, cobalt, and zinc; also from sesquioxide of iron, if the quantity of the latter is not too considerable.

The phosphoric acid is precipitated as phosphate of binoxide of tin, according to § 134, *b*, *δ*, *aa*. The filtrate contains the bases free from any foreign body requiring removal, which, of course, greatly facilitates their estimation.* REISSIG obtained very satisfactory results by this method. In separating phosphoric acid in the presence of sesquioxide of iron and alumina by means of tin, GIRARD's process (§ 134, *b*, *δ*, *bb*) should be adopted.

β. From sesquioxide of iron, alumina, alkaline earths, and all other oxides not precipitable by carbonate of baryta (H. ROSE).

Mix the hydrochloric acid solution—after removing the free acid as far as practicable by evaporation, and subsequently neutralizing it partly by carbonate of soda—with carbonate of baryta in excess, let the mixture digest some days in the cold, filter, and wash with cold water. The precipitate contains the whole of the phosphoric acid in combination with sesquioxide of iron, alumina, baryta, and also the excess of carbonate of baryta used. The other bases are in the filtrate. The precipitate is dissolved in the least possible quantity of dilute hydrochloric acid, the baryta cautiously precipitated with sulphuric acid and filtered off, the filtrate saturated with carbonate of soda, and evaporated to dryness with the precipitate in it; the residue is mixed with an equal quantity of pure silicic acid, and six times as much carbonate of soda, and the mixture heated in a large platinum crucible, commencing with a gentle heat, which is then gradually increased to a very high degree of intensity. The remaining operations are conducted exactly as directed in *c*, *β*.

γ. From sesquioxide of iron in large proportion and in presence of alkaline earths (FRESENIUS†).

The determination of the phosphoric acid in such compounds may, indeed, be accomplished by the method given in § 134, *d*, but the separation by these methods, of a small quantity of phosphoric acid from a very large proportion of sesquioxide of iron is a most tedious operation; it is therefore preferable in cases of the kind to proceed as follows: the hydrochloric acid solution is heated to boiling, then removed from the lamp, and solution of sulphite of soda added, until carbonate of soda produces a nearly white precipitate; the mixture is then boiled until the odor of sulphurous acid has gone off; the excess of free acid which might still be present is nearly neutralized with carbonate of soda, a few drops of chlorine water are added, and lastly, acetate of soda in excess. The minutest quantity of phosphoric acid shows itself at once by the formation of a white precipitate of phosphate of sesquioxide of iron.* More chlorine water is now added, drop by drop, until the fluid appears reddish; it is then boiled until the precipitate has well subsided; the latter is filtered off hot, and washed with hot water mixed with a little acetate of ammonia. The precipitate contains the whole of the phosphoric acid, together with a small portion of the iron; the filtrate contains the greater portion of the latter, together with the alkaline earths. The precipitate is treated as directed in *l*, that is, the phosphoric acid is first separated from the nitric acid solution by molybdate of ammonia, and the iron and alumina are then precipitated from the filtrate by sulphide of ammonium. If the precipitate is free from alumina, it may also be ignited, weighed, and the iron in it determined in the volumetric way (§ 113), in which case the phosphoric acid is found from the loss. This method may be varied in many ways; thus the sesquichloride of iron may be reduced by sulphuretted hydrogen, the excess of the latter being expelled by carbonic acid, and again the precipitation of the phosphate of iron may be effected by digestion with carbonate of lime (free from phosphoric acid). If you precipitate the phosphate of iron by sesquicarbonate of ammonia you must do so at a temperature below 21°, otherwise a little phosphoric acid will remain in the filtrate (SPILLER†).

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* If the nitric acid is not concentrated, a little nitrate of protoxide of tin is formed, which dissolves and must afterwards be precipitated from the acid fluid by sulphuretted hydrogen. BABER, Zeitschr. f. d. ges. Naturwiss. 1864, 324.

† Journ. f. prakt. Chem. 45, 258.

i. From the Metals of the Fifth and Sixth Groups.

Dissolve in hydrochloric or nitric acid, precipitate with sulphuretted hydrogen, filter, determine the bases by the methods given in §§ 115 to 127, and the phosphoric acid in the filtrate by the method described § 134, *b*, *a*. From oxide of silver the phosphoric acid is separated in a more simple way still, by adding hydrochloric acid to the nitric acid solution; from oxide of lead it is separated most readily by the method described in *b*.

k. From all Bases, except the Oxides of Mercury (H. ROSE).

The phosphoric acid is separated as phosphate of suboxide of mercury by ROSE's method (§ 134, *b*, γ).

a. If the substance is free from iron and alumina, the filtrate from the phosphate of suboxide of mercury contains all the bases as nitrates, together with much nitrate of suboxide of mercury, and occasionally also some oxide. The former is removed by the addition of hydrochloric acid. The precipitated subchloride of mercury is free from other bases. If only a slight precipitate is produced by hydrochloric acid, add ammonia before filtering. The bases in the filtrate are determined in the usual way. If the mercury has been separated by ammonia, the precipitate is dried and ignited (under a chimney with good draught). Should a residue remain, this must be examined. If it consists of phosphates of the alkaline earths, the treatment with mercury and nitric acid must be repeated; if, on the contrary, it consists of pure magnesia or of carbonates of the alkaline earths, it is dissolved in hydrochloric acid, and the solution added to the fluid containing the chief portion of the bases. The following method is often advantageously resorted to instead of the one described: the filtrate from the phosphate of suboxide of mercury is evaporated to dryness, in a platinum dish, and the residue ignited, in a platinum crucible, under a chimney with good draught. If alkaline nitrates are present, some carbonate of ammonia must be added from time to time during the process of ignition, to guard against injury to the crucible from the formation of caustic alkali. The ignited residue is treated, according to circumstances, first with water and then with nitric acid, or at once with nitric acid.

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* Silicic acid and arsenic acid produce a similar precipitate, and must therefore, if present, be previously removed.

† Journ. of Chem. Soc. (2) 4, 148.

β. *If the substance contains iron but not alumina*, the greater part of the iron is left undissolved with the phosphate of suboxide of mercury. The dissolved part is separated from the other bases by the methods given in Section V.; the undissolved part is obtained, after ignition of the residue with carbonate of soda and potassa and treating the ignited mass with water, as sesquioxide of iron containing alkali (and generally also some phosphoric acid). This is dissolved in hydrochloric acid, and precipitated with ammonia.

γ. *If the substance contains alumina* the process just given cannot be used, as phosphate of alumina is not decomposed by fusion with carbonated alkali, while nitrate of alumina, like nitrate of sesquioxide of iron, is decomposed by simple evaporation. In this case proceed as follows: Dissolve the substance in the least quantity of nitric acid, precipitate hot with nitrate of suboxide of mercury, add a little nitrate of protoxide of mercury, and then pure potash or soda, till a permanent red precipitate appears. The precipitate contains no alumina, it is to be treated according to *a* or *β* (H. Rose, E. E. Munroe*).

l. From all Bases without exception.

Apply Sonnenschein's method (§ 134, *b*, *β*), and in the filtrate from the phospho-molybdate of ammonia separate the bases from the molybdic acid. As molybdic acid comports itself with sulphuretted hydrogen and sulphide of ammonium like a metal of the sixth group, it is best to precipitate metals of the sixth and also of the fifth group from acid solution with sulphuretted hydrogen, before proceeding to precipitate the phosphoric acid with molybdic acid; the latter will then have to be separated only from the metals of the first four groups. This is done in the following manner: mix the acid fluid, in a flask, with ammonia till it acquires an alkaline reaction, add sulphide of ammonium in sufficient excess, close the mouth of the flask, and digest the mixture. As soon as the solution appears of a reddish-yellow color, without the least tint of green, filter off the fluid, which contains sulphide of molybdenum and ammonium, wash the residue with water mixed with some sulphide of ammonium, and separate the remaining metallic sulphides and hydrated oxides of the fourth and third groups by the methods which will be found in Section V. Mix the filtrate cautiously with hydrochloric acid in moderate excess, remove the sulphide of molybdenum according to § 128, *d*, and determine the alkaline earths and alkalies in the filtrate.

This method of separating the phosphoric acid from the bases is highly to be recommended; especially in cases where a small quantity of phosphoric acid has to be determined in presence of a very large quantity of sesquioxide of iron and alumina, as, for example, in iron ores, soils, &c. As arsenic acid and silicic acid give, with molybdic acid and ammonia, similar yellow precipitates, it is necessary, if these acids are present, to remove them first.

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* Amer. Journ. of Sci. and Arts, May, 1871; Zeitschr. f. anal. Chem. 10, 467.

As the separation of the bases from the large excess of molybdic acid used is somewhat tedious, the best way is to arrange matters so that this process may be altogether dispensed with. Supposing, for instance, you have a fluid containing sesquioxide of iron, alumina, and phosphoric acid, estimate, in one portion, by cautious precipitation with ammonia, the total amount of the three bodies; in another portion the phosphoric acid, by means of molybdic acid; and in a third, the sesquioxide of iron, in the volumetric way. The difference gives the alumina. I have already called attention (*h*, *γ*) to a method which is often very convenient, and which consists in first separating the phosphoric acid with a small part of the iron, and then determining the acid with the iron and alumina in this precipitate. In this way you have merely to separate the molybdic acid from the minute quantity of iron and the alumina, and not from other bases, which greatly simplifies the process.

§ 136.

2. Boracic Acid.

I. *Determination.*

Boracic acid is estimated either *indirectly* or in the form of *borofluoride of potassium.*

1. The determination of the boracic acid in an aqueous or alcoholic solution cannot be effected by simply evaporating the fluid and weighing the residue, as a notable portion of the acid volatilizes and is carried off with the aqueous or alcoholic vapor. This is the case also when the solution is evaporated with oxide of lead in excess.

a. Mix the solution of the boracic acid with a weighed quantity of perfectly anhydrous pure carbonate of soda, in amount about $1\frac{1}{2}$ times the supposed quantity of the boracic acid present. Evaporate the mixture to dryness, heat the residue to fusion, and weigh. The residue contains a known amount of soda, and unknown quantities of carbonic acid and boracic acid. Determine the carbonic acid by one of the methods given in § 139, and find the boracic acid from the difference (H. Rose).

b. In the method *a*, if between 1 and 2 eq. carbonate of soda are used to 1 eq. boracic acid—and this can easily be done if one knows approximately the amount of the latter present—all the carbonic acid is expelled by the boracic acid. Hence we have only to deduct the NaO from the residue to find the BO_3. As the tumultuous escape of carbonic acid may lead to loss, it is well, after having thoroughly dried the residual saline mass, to project it in small portions cautiously into the red-hot crucible. Results good (F. G. Schaffgotsch).*

c. When the amount of acid is quite unknown, and an estimation of carbonic acid in the residue is objected to, you may proceed thus. Evaporate the solution of the acid with addition of a weighed quantity of anhydrous neutral borax free from carbonic acid to dryness, and heat the residue to redness with great caution (on account of the intumescence) till the weight is constant. The amount of neutral borax must be so adjusted that it may not be entirely converted into biborate of soda (H. Rose).

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* Pogg. Ann. 107, 427.

d. If a solution contains besides boracic acid, only alkalies or magnesia, the acid may be determined, according to C. Marignac,* in the following manner:—Neutralize the solution with hydrochloric acid, add double chloride of magnesium and ammonium in such quantity that 1 part of boracic acid may have at least 2 parts of magnesia, then add ammonia and evaporate to dryness. If a precipitate is formed on adding the ammonia which does not redissolve readily on warming, add more chloride of ammonium. The evaporation is conducted, at least towards the end, in a platinum dish, a few drops of ammonia being added from time to time. Ignite the dry mass, treat with boiling water, collect the insoluble precipitate (consisting of borate of magnesia mixed with excess of magnesia) on a filter, and wash with boiling water till the washings remain clear with nitrate of silver. The filtrate and washings are mixed with ammonia, evaporated to dryness, ignited, and washed with boiling water as before.

The two insoluble residues are ignited together in the platinum dish before used, as strongly as possible, and for a sufficiently long time, in order to decompose the slight traces of chloride of magnesium that might still be present. After weighing determine the magnesia and find the boracic acid from the difference. The estimation of the magnesia may be made by dissolving the residue in hydrochloric acid and precipitating as phosphate of magnesia and ammonia, or more quickly, and almost as accurately, by dissolving in a known quantity of standard sulphuric acid at a boiling temperature and determining the excess of acid with standard soda (comp. Alkalimetry).

Should a little platinum remain behind on dissolving the residue, it must be weighed and subtracted from the weight of the whole (unless the dish was weighed first). Results satisfactory. Marignac obtained in two experiments ·276 instead of ·280.

2. If boracic acid is to be determined as *borofluoride of potassium*, alkalies only (preferably only potash) may be present. The process is conducted as follows:—Mix the fluid with pure solution of potassa, adding for each eq. boracic acid supposed to be present, at least 1 eq. potassa; add pure hydrofluoric acid (free from silicic acid) in excess, and evaporate, in a platinum dish, on the water-bath, to dryness. The fumes from the evaporating fluid should redden litmus paper, otherwise there is a deficiency of hydrofluoric acid. The residue consists now of KF,BF_3 and KF,HF. Treat the dry saline mass, at the common temperature, with a solution of 1 part of acetate of potassa in 4 parts of water, let it stand a few hours, with stirring, then decant the fluid portion on to a weighed filter, and wash the precipitate repeatedly in the same way, finally on the filter, with solution of acetate of potassa, until the last rinsings are no longer precipitated by chloride of calcium. By this course of proceeding, the hydrofluate of fluoride of potassium is removed, without a particle of the borofluoride of potassium being dissolved. To remove the acetate of potassa, wash the precipitate now with spirit of wine of 78 per cent., dry at 100°, and weigh. As

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* Zeitschr. f. anal. Chem. 1, 405.

chloride of potassium, nitrate and phosphate of potassa, salts of soda, and even, though with some difficulty, sulphate of potassa, dissolve in solution of acetate of potassa, the presence of these salts does not interfere with the estimation of the boracic acid; however, salts of soda must not be present in considerable proportion, as fluoride of sodium dissolves with very great difficulty. The results obtained by this method are satisfactory. STROMEYER's experiments gave from 97·5 to 100·7 instead of 100. When the amount of alkali salt to be removed is very large, the saline mass left on evaporation should be warmed with the solution of acetate of potassa, allowed to stand 12 hours in the cold and then filtered. In this way the quantity of acetate of potassa required will be much reduced. For the composition and properties of borofluoride of potassium, see § 93, 5. As the salt is very likely to contain silicofluoride of potassium it is indispensable to test it for that substance; this is done by placing a small sample of it on moist blue litmus paper, and putting another sample into cold concentrated sulphuric acid. If the blue paper turns red, and effervescence ensues in the sulphuric acid, the salt is impure, and contains silicofluoride of potassium. To remove this impurity, dissolve the remainder of the salt, after weighing it, in boiling water, add ammonia, and evaporate, redissolve in boiling water, add ammonia, &c., repeating the same operation at least six times. Finally, after warming once more with ammonia, filter off the silicic acid, evaporate to dryness, and treat again with solution of acetate of potassa and alcohol (A. STROMEYER).[*] I was obliged to modify STROMEYER's method for effecting the separation of the silicic acid, the results of my experiments having convinced me that treating the salt only once with ammonia, as recommended by that chemist, is not sufficient to effect the object in view.

II. *Separation of Boracic Acid from the Bases.*

a. From the Alkalies.

Dissolve a weighed quantity of the borate in water, add an excess of hydrochloric acid, and evaporate the solution on the water-bath. Towards the end of the operation add a few more drops of hydrochloric acid, and keep the residue on the water-bath, until no more hydrochloric acid vapors escape. Determine now the chlorine in the residue (§ 141), calculate from this the alkali, and you will find the boracic acid from the difference.

E. SCHWEIZER, with whom this method originated, states that it gave him very satisfactory results in the analysis of borax. It will answer also for the estimation of the bases in the case of some other borates. It is self-evident that the boracic acid may be estimated, in another portion of the salt, by I., 1, *c*, or 2. If you have to estimate boracic acid in presence of large proportions of alkaline salts, make the fluid alkaline with potassa, evaporate to dryness, extract the residue with alcohol and some hydrochloric acid, add solution of potassa to strongly alkaline reaction, distil off the spirit of wine, and then proceed as in I., 1, *c*, or 2 (AUG. STROMEYER, *loc. cit.*)

LUNGE[†] determined the soda in boronatrocalcite alkalimetrically, by dissolving the mineral in normal nitric acid (§ 215) and titrating back with normal soda, till the tint of the litmus added becomes violet.

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[*] Annal. d. Chem. u. Pharm. 100, 82.

[†] *Ib.*, 138, 53.

b. From Lime.

Dissolve in hydrochloric acid in the heat, avoiding too large an excess, neutralize with ammonia and precipitate with oxalate of ammonia (LUNGE, *loc. cit.*).

c. From almost all other Bases except Alkalies.

The compounds are decomposed by boiling or fusing with carbonate or hydrate of potassa; the precipitated base is filtered off, and the boracic acid determined in the filtrate, according to I., 1 *d.*, or 2. If magnesia was present, a little of this is very likely to get into the filtrate, and—if process I, 2, is employed—upon neutralizing with hydrofluoric acid, this separates an insoluble fluoride of magnesium, which may either be filtered off at once, or removed subsequently, by treating the borofluoride of potassium with boiling water, in which that salt is soluble, and the fluoride of magnesium insoluble.

d. From the Metallic Oxides of the Fourth, Fifth, and Sixth Groups.

The metallic oxides are precipitated by sulphuretted hydrogen, or, as the case may be, sulphide of ammonium,* and determined by the appropriate methods. The quantity of boracic acid may often be inferred from the loss. If it has to be estimated in the direct way, the filtrate, after addition of solution of potassa and some nitrate of potassa, is evaporated to dryness, the residue ignited, and the boracic acid estimated by I., 1 *d.*, or 2. In cases where the metal has been precipitated by sulphuretted hydrogen from acid or neutral solutions, the boracic acid may also be determined in the filtrate—in the absence of other acids—by I., 1 *a* or *b* or *c*, after the complete removal of the sulphuretted hydrogen by transmitting carbonic acid through the fluid.

e. From the whole of the Fixed Bases.

A portion of the very finely pulverized substance is weighed, put into a capacious platinum dish, and digested with a sufficient quantity of hydrofluoric acid (which leaves no residue when evaporated in a platinum dish); pure concentrated sulphuric acid is then gradually added, drop by drop, and the mixture heated, gently at first, then more strongly, until the excess of the sulphuric acid is completely expelled. In this operation the boracic acid goes off in the form of fluoride of boron ($BO_3 + 3HF = BF_3 + 3HO$). The residue contains the bases in the form of sulphates; the bases are determined by the appropriate methods, and the quantity of the boracic acid is found by difference. It is of course taken for granted that the substance is decomposable by sulphuric acid.

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* Boracic acid cannot be separated completely from alumina by precipitation of the hydrochloric acid solution with sulphide of ammonium or with carbonate of ammonia (WOHLER) Ann. d. Chem. u. Pharm. 141, 268.

§ 137.

3. OXALIC ACID.

I. *Determination.*

Oxalic acid is either precipitated as *oxalate of lime*, and the latter determined as *carbonate of lime*, *lime*, or *sulphate of lime*; or the amount contained in a compound is inferred from the quantity of solution of permanganate of potassa required to effect its conversion into carbonic acid; or from the quantity of gold which it reduces; or from the amount of carbonic acid which it yields upon accession of 1 eq. oxygen.

a. Determination as Carbonate of Lime, &c.

Precipitate with solution of acetate of lime, added in moderate excess, and treat the precipitated oxalate of lime as directed in § 103. If this method is to yield accurate results, the solution must be neutral or slightly acid with *acetic acid*; it must not contain alumina, sesquioxide of chromium, or oxides of the heavy metals, more especially sesquioxide of iron or oxide of copper; therefore, where these conditions do not exist, they must first be supplied.

b. Determination by means of Solution of Permanganate of Potassa.

Standardize the solution of permanganate of potassa, as directed § 112, 2 *a*, *cc*, by means of oxalic acid; then dissolve the substance in about 150 c.c. water, or acid and water (sulphuric acid is the best acid to use); add, if necessary, a further quantity of sulphuric acid, (about 6 or 8 c.c. strong sulphuric acid should be present), heat to about 60°, and then run in the permanganate, with constant stirring, until the fluid just shows a red tint. Knowing the quantity of oxalic acid which 100 c.c. of the standard permanganate will oxidize, a simple calculation will give the quantity of oxalic acid corresponding to the c.c. of permanganate used in the experiment. The results are very accurate.

c. Determination from the reduced Gold (H. ROSE).

α. In compounds soluble in water. Add to the solution of the oxalic acid or the oxalate a solution of sodio-terchloride, or ammonio-terchloride of gold, and digest for some time at a temperature near ebullition, with exclusion of direct sunlight. Collect the precipitated gold on a filter, wash, dry, ignite, and weigh. 1 eq. gold (196·71) corresponds to 3 eq. C_2O_3 (3 + 36 = 108).

β. In compounds insoluble in water. Dissolve in the least possible amount of hydrochloric acid, dilute with a very large quantity of water, in a capacious flask, cleaned previously with solution of soda; add solution of gold in excess, boil the mixture some time, let the gold subside, taking care to exclude sunlight, and proceed as in *α*.

d. Determination as Carbonic Acid.

This may be effected either,

α. By the method of organic analysis; or

β. By mixing the oxalic acid or oxalate with finely pulverized binoxide of manganese in excess, and adding sulphuric acid to the mixture, in an apparatus so constructed that the disengaged carbonic acid passes off perfectly dry. The theory of this method may be illustrated by the following equation: $C_2O_3 + MnO_2 + SO_3 = MnO,SO_3 + 2CO_2$. For each 1 eq. oxalic acid we obtain accordingly 2 eq. carbonic acid. For the apparatus and process, I refer to the chapter on the examination of manganese ores, in the Special Part of this work. Here I may remark that free oxalic acid must first be prepared for the process by slight supersaturation with alkali free from carbonic acid, and also that 9 parts of anhydrous oxalic acid require theoretically 11 parts of (pure) binoxide of manganese. Since an excess of the latter substance does not interfere with the accuracy of the results, it is easy to find the amount to be added. The binoxide of manganese need not be pure, but it must contain no carbonate. This method is expeditious, and gives very accurate results, if the process is conducted in an apparatus sufficiently light to admit of the use of a delicate balance. Instead of binoxide of manganese, chromate of potassa may be used (compare § 130, 1 *d*), and instead of estimating the carbonic acid by loss it may be collected in a weighed soda-lime tube (§ 139, *e*); the latter method is always to be preferred in the case of small quantities.

II. *Separation of Oxalic Acid from the Bases.*

The most convenient way of analysing oxalates is, in all cases, to determine in one portion, the acid, by one of the methods given in I., in another portion, the base, particularly as the latter object may be generally effected by simple ignition in the air, which reduces the salt either to the metallic state (*e.g.*, oxalate of silver), or to pure oxide (*e.g.*, oxalate of lead), or to carbonate (*e.g.*, the oxalates of the alkalies and alkaline earths). In many cases, especially where the base is reduced by carbonic oxide and where the corresponding carbonate does not give up its carbonic acid at all on ignition or only with difficulty, it is better to fuse with vitrified borax (compare § 139, II., *c*). The increase of weight in the platinum crucible containing the borax after fusion corresponds to the amount of base present; the loss of weight corresponds to the oxalic acid, or, as the case may be, to the oxalic acid and water.

If acid and base have to be determined in one and the same portion of the oxalate, the following methods may be resorted to:

a. The oxalic acid is determined by I., *c*, and the gold separated from the bases in the filtrate by the methods given in Section V.

b. In many soluble salts the oxalic acid may be determined by the method I., *a*; separating the bases afterwards from the excess of the salt of lime by the methods given in Section V.

c. Many oxalates whose bases are precipitated by carbonate of potassa or carbonate of soda, and are insoluble in an excess of the precipitant, may be decomposed by boiling with an excess of solution of carbonate of potassa or carbonate of soda, oxide or carbonate being formed on the one, and alkaline oxalate on the other side.

d. All salts of oxalic acid with the oxides of the fourth, fifth, and sixth groups, may be decomposed with sulphuretted hydrogen, or sulphide of ammonium.

§ 138.

4. HYDROFLUORIC ACID.

I. *Determination.*

Free hydrofluoric acid in aqueous solution* is determined either with standard alkali or as *fluoride of calcium*. In the latter case carbonate of soda is added in moderate excess, then the solution being boiled, chloride of calcium is added as long as a precipitate continues to form; when the precipitate, which consists of fluoride of calcium and carbonate of lime, has subsided, it is washed, first by decantation, afterwards on the filter, and dried; when dry, it is ignited in a platinum crucible (§ 53); water is then poured over it, in a platinum or porcelain dish, acetic acid added in slight excess, the mixture evaporated to dryness on the water-bath, and heated on the latter until all odor of acetic acid disappears. The residue, which consists of fluoride of calcium and acetate of lime, is heated with water, the fluoride of calcium filtered off, washed, dried, ignited (§ 53), and weighed. As a control of the purity of the fluoride of calcium it is well to convert it after weighing into sulphate. If the precipitate of fluoride of calcium and carbonate of lime were treated with acetic acid, without previous ignition, the washing of the fluoride would prove a difficult operation. Presence of nitric or hydrochloric acid in the aqueous solution of the hydrofluoric acid does not interfere with the process (H. ROSE).

II. *Separation of Fluorine from the Metals.*

1. *Fluorides Soluble in Water.*

If the solutions have an acid reaction, carbonate of soda is added in excess. If there is an odor of ammonia now, heat till the latter is expelled. If the carbonate of soda produces no precipitate, the fluorine is determined by the method given in I., and the bases in the filtrate are separated from the excess of lime, and from the soda, by the methods given in Section V. But if the carbonate of soda produces a precipitate, the mixture is heated to boiling, then filtered, and the fluorine determined in the filtrate by the method given in I.; the base is in the residue, which must, however, first be tested, to make sure that it contains no fluorine. Neutral solutions are mixed with a sufficient quantity of chloride of calcium, and the mixture heated to boiling, in a platinum dish or, but less appropriately, in a porcelain dish; the precipitate of fluoride of calcium is allowed to subside, thoroughly washed with hot water by decantation, transferred to the filter, dried, ignited, and weighed. The bases in the filtrate are then separated from the excess of the salt of lime by the usual methods. That the bases may be determined also in separate portions by the methods given in *b*, need hardly be stated.

2. *Insoluble Fluorides.*

a. Decomposition by Sulphuric Acid (Indirect Estimation of the Fluorine).

α. Anhydrous Compounds.

The finely pulverized and weighed substance is heated for some time with pure concentrated sulphuric acid, and finally ignited until the free sulphuric acid is completely expelled. In the presence of alkalies carbonate of ammonia must be added during the ignition. The residuary sulphate is weighed, and the metal contained in it calculated; the fluorine is estimated by loss. In cases where we have to deal with a metal whose sulphate gives off part of the sulphuric acid upon ignition, or where the residue contains several metals, it is necessary to subject the residue to analysis before this calculation can be made. In the case of many compounds, for instance of fluoride of aluminium (which after ignition requires prolonged heating with sulphuric acid for its decomposition), long continued strong ignition does not leave the sulphate, but the base in a pure state. Topaz (a silicate of alumina in isomorphous mixture with silicofluoride of aluminium) is not decomposed by boiling sulphuric acid, but it is decomposed by fusion with bisulphate of potassa.

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* In analysing fluorides you must always avoid bringing acid solutions in contact with glass or porcelain. If platinum or silver dishes of sufficient size are not at hand you may sometimes use gutta-percha vessels, or glass vessels coated with wax or paraffin.

β. Hydrated Fluorides.

A sample of the substance is heated in a tube.

aa. The Water expelled does not redden Litmus Paper. The water is determined by ignition; the fluorine and metal as directed in *a*, *a*.

bb. The Water expelled has an acid reaction. The substance is treated with sulphuric acid as directed in *a*, *a*, to determine the metal on the one hand, and the water + fluorine on the other. Another weighed portion is then mixed, in a small retort, with about 6 parts of recently ignited oxide of lead; the mixture is covered with a layer of oxide of lead, the retort weighed, and the water expelled by the application of heat, increased gradually to redness. No hydrofluoric acid escapes in this process. The weight of the expelled water is inferred from the loss. The first operation having given us the water + fluorine, and the second, the water alone, the difference is consequently the fluorine.

b. Decomposition by Fusion with Alkaline Carbonates.

Many insoluble fluorides, fluoride of aluminium for instance, may be completely decomposed by fusion with alkaline carbonate alone, others, such as fluoride of calcium, require the addition of silicic acid. In the first case the fluorine is estimated in the aqueous solution of the fusion according to I., in the latter according to § 166, 5. The temperature must not be too high, or some alkaline fluoride may be lost.

3. *Fluorides completely Decomposable by Sulphuric Acid.*

As might be inferred from 2, almost all fluorides are decomposed by heating with sulphuric acid with evolution of hydrofluoric acid. If silica or a silicate is added to the fluoride in sufficient quantity, fluoride of silicon and water escape instead of hydrofluoric acid: $SiO_2 + 2HF = Si F_2 + 2HO$. On this reaction two methods of estimating fluorine are based. In the first, which I published some years ago,* the fluoride of silicon is determined by the increase in weight of absorption tubes; this I believe to be in many cases the only method which is applicable, and when carefully carried out it yields the most accurate results. In the second method the fluoride of silicon is determined by the loss of weight of the evolution apparatus or of glass.

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* Zeitschr. f. anal. Chem. 5, 190.

a. Estimation by Absorption of the evolved Fluoride of Silicon.

The method as here given is the result of a long series of experiments; the conditions laid down must be most carefully attended to. The fluoride must be in the finest powder. As silicic acid we use

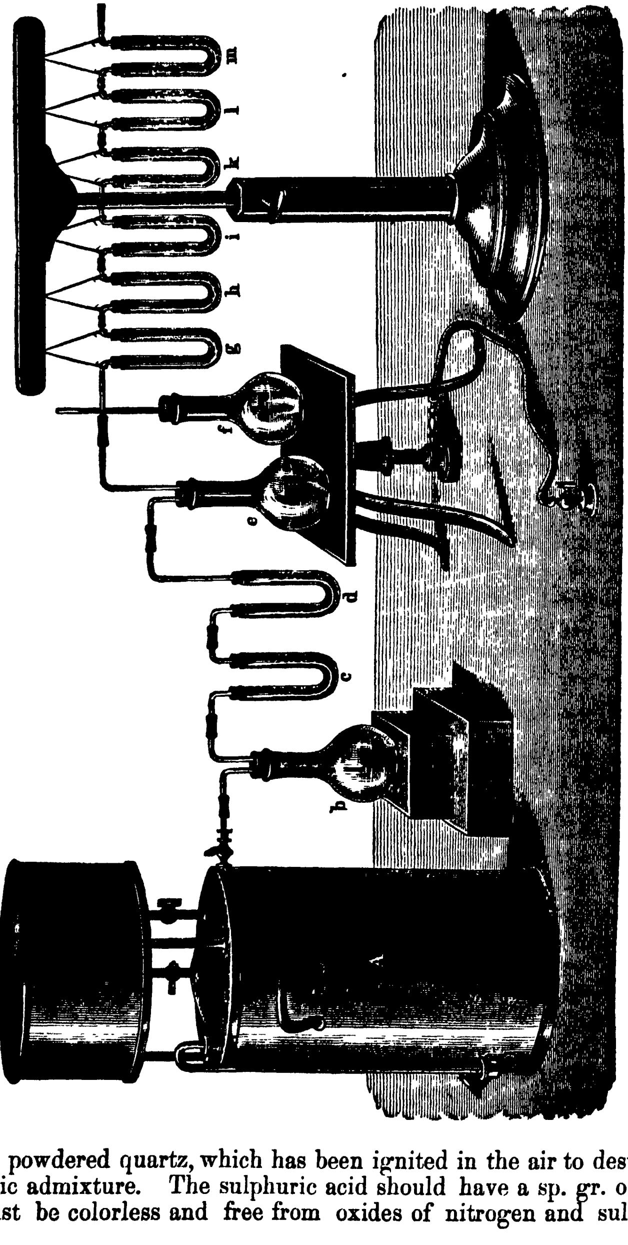

Fig. 87.

finely powdered quartz, which has been ignited in the air to destroy any organic admixture. The sulphuric acid should have a sp. gr. of 1·848, it must be colorless and free from oxides of nitrogen and sulphurous acid. The gasometer must be filled with clean air, and not with air from the laboratory, for any dust of organic matter, traces of coal gas, &c., would interfere with the accuracy of the result. The apparatus required is shown fig. 87. *A* contains atmospheric air, *b* is half filled with sulphuric acid, *c* contains soda-lime with plugs of wool, *d* pieces of glass moistened with sulphuric acid. The air is thus freed from carbonic acid and suspended matter, and dried by sulphuric acid (p. 57). *e* is the decomposing flask, it has a capacity of about 250 c.c. *f* is half filled with sulphuric acid, its cork, which should not fit air-tight, bears a thermometer whose bulb dips into the acid. *e* and *f* should be so placed on the iron plate that the temperature in both may be equal. *g* is empty; *h* contains fused chloride of calcium in the first limb, and pumice impregnated with anhydrous sulphate of copper in the second. These U-tubes serve to retain the small amount of sulphuric acid and the hydrochloric acid which may accompany it. The chloride of calcium and the sulphate of copper must both be anhydrous, or they will decompose and retain fluoride of silicon. *i*, *k*, and *l* are the weighed absorption tubes; they are 10 or 12 cm. high, and about 12 mm. wide. *i* contains in the first limb pumice moistened with water between plugs of wool, in the bend and half of the second limb soda-lime, in the upper half of the second limb fused chloride of calcium between plugs of wool. The tube after being charged weighs about 40 or 50 grm. *k* completes the absorption; it is filled half with soda-lime and half with fused chloride of calcium. *l* takes up again the small amount of water carried away from *i* and *k*; the bend is filled with pieces of glass moistened with sulphuric acid. These absorption tubes retain the fluoride of silicon, the carbonic acid which may be possibly evolved from the soda-lime by hydrofluosilicic acid, and the aqueous vapor; and the air escapes through the unweighed guard tube *m* into the atmosphere. The latter contains in the first limb chloride of calcium, in the second soda-lime. The flexible connexions should not be long, and should be washed and dried before use.

When the apparatus has been tested and found air-tight, place the weighed and very finely divided substance in *e*. The substance should be free from carbonic acid (§ 166, 8), and the quantity taken should give not less than ·1 grm. fluoride of silicon if possible. Add for every part of fluoride supposed to be present 10 or 15 parts of finely powdered quartz (previously strongly ignited in the air), and then 40 or 50 c.c. pure concentrated sulphuric acid. Connect *e*, on the one hand, with *d*, and, on the other, with *g*, and pass a moderate current of air, which should enter the fluid in the decomposing flask from the bottom. Heat the iron plate, shake *e* frequently and raise the temperature very gradually, till the thermometer in *f* indicates 150° to 160°. The commencement of the decomposition shows itself not only by the appearance of bubbles of gas in the fluid, more particularly at the edge, but also by the separation of hydrated silica in *i*. The bubbles of gas will disappear on shaking the fluid; as soon as they cease to form again remove the lamp; the time usually occupied in the decomposition is one hour for small quantities of fluoride (·1 grm.), two or three hours for large quantities (1 grm.) After a while shut off the current of air, remove the weighed tubes *i*, *k*, and *l*, and during the weighing of these connect *h* with *m* by means of a glass tube. After weighing replace *i*, *k*, and *l*, heat again to 150 or 160°, and pass the air again for half an hour or an hour, weighing *i*, *k*, and *l* again. If any alteration of weight has occurred, the process must be continued.

The increase in weight of the absorption tubes, after deducting ·001 grm. for every hour during which the air has been passing (*i.e.*, for every 6 litres of air) represents the amount of fluoride of silicon. The small correction is necessary because air, even when it comes in contact only with short washed pieces of india-rubber, always gives traces of sulphurous and carbonic acid when passed through hot concentrated sulphuric acid. The results thus obtained are very satisfactory, and differ from the truth at the most by a few milligrammes.

b. Other methods of Estimating the Fluoride of Silicon expelled.

α. Method of WÖHLER. Only applicable when the substance is readily decomposed by sulphuric acid, and the amount of fluorine is large. Transfer the very finely divided substance, if necessary, intimately mixed with 10 or 15 parts of ignited quartz powder to a small flask, add pure sulphuric acid, close quickly with a cork fitted with a small tube filled with fused chloride of calcium (or better still, half with fused chloride of calcium and half with anhydrous sulphate of copper on pumice), weigh the whole apparatus as quickly as possible, warm it till no more fumes of fluoride of silicon escape, remove the last particles of gas in the apparatus by an air pump, allow to cool, and weigh. The loss of weight indicates the amount of fluoride of silicon.

β. Regarding the methods of F. v. KOBELL* and ZALESKY,† depending on the loss of weight of Bohemian glass of known composition, I must remark that no direct proofs have been given of their accuracy.

Fourth Division of the First Group of the Acids.

CARBONIC ACID—SILICIC ACID.

§ 139.

1. CARBONIC ACID.

I. *Determination.*

a. In a mixture of Gases.

After thoroughly drying the gases with a ball of chloride of calcium, or saturating with moisture (§ 16), measure them accurately in a graduated tube over mercury, insert a ball of hydrate of potassa,‡ cast on a platinum wire in a pistol bullet-mould, take care that the end of the platinum wire remains under the surface of the mercury, leave in the tube for 24 hours, or until the volume of the gas ceases to show further diminution; withdraw the ball, and measure the gas remaining, re-insert the same or a fresh ball of potassa, and repeat till no further absorption takes place. The carbonic acid gas is inferred from the difference, provided the gaseous mixture contained no other gas liable to absorption by potassa (compare §§ 12–16 and 198). In very accurate analyses you must bear in mind that carbonic acid does not exactly follow the law of MARIOTTE (§ 198, β).

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* Journ. f. prakt. Chem. 92, 385. † Zeitschr. f. anal. Chem. 5, 205.

‡ The ordinary hydrate is not adapted for the purpose. It should be fused with a quarter of its weight of water in a platinum crucible.

If the amount of carbonic acid is very small, this process does not yield sufficiently accurate results. In such cases one of the methods recommended in "The Analysis of Atmospheric Air" should be employed. Several kinds of special apparatus are in use for the estimation of carbonic acid in coal gas and for the purposes of sugar works. I may mention those proposed by F. RÜDORFF* and LEHMANN and H. WAHLERT† for the first purpose, and by C. SCHEIBLER‡ and C. STAMMER§ for the second. Besides these volumetric methods the gravimetric processes given by myself for the analysis of gaseous mixtures|| may often be used with great advantage. These will be found in the Special Part.

b. In Aqueous Solution.

a. WITH HYDRATE OF LIME.

Into a flask, holding about 300 c.c., put 2·5 to 3 grm. hydrate of lime perfectly free from carbonate.¶ If you cannot get any lime pure enough, determine the carbonic in it according to II., *e*, weigh the quantity taken, and deduct the carbonic acid in it from the result. Provide the flask with a good india-rubber stopper, tare or weigh exactly, add the carbonic acid water with gentle agitation till the flask is two-thirds or three-quarters full, and close at once.

In adding the carbonic acid water every care must of course be taken to guard against loss of carbonic acid. If the water flows from a pipe, it is allowed simply to run in. If it is in a jug or bottle, cool it to 4°, and transfer the quantity required with a syphon.** If the water is in a basin or well, provide the flask with an arrangement like that shown in fig. 88, dipping the flask into the water, till the upper opening of *a b* is under the surface. As the water enters through this tube, and its carbonic acid immediately combines with the lime, the air escapes by *c d*. Water which is not very rich in free carbonic acid may be removed from the basin or well by a plunging-syphon.

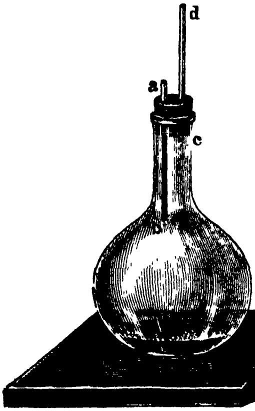

Fig. 88.

Now weigh the flask with its stopper again, and you will find the quantity of water taken. No way of measuring the water is so accurate in retaining all the carbonic acid and in giving the quantity of water taken.

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* Pogg. Annal. 125, 71. † Zeitschr. f. anal. Chem. 7, 58.
‡ Dingler's polyt. Journ. 183, 306. § *Ib.* 102, 368.
|| Zeitschr. f. anal. Chem. 3, 343.

¶ This is prepared by slaking freshly burnt lime with water in such a manner that the hydrate obtained appears dry and pulverulent. It is preserved in small bottles, the corks or stoppers of which are covered with sealing wax.

** If the water is poured directly from the jug into the flask, carbonic acid gas is very likely to get into the latter as well as the water.

If there is much interval between the mixing of the water and the lime and the estimation of the carbonic acid in the precipitate the carbonate of lime which is at first amorphous passes spontaneously into the crystalline condition; but if the carbonic acid is to be determined soon after the mixing, heat for some time on the water bath, raising the stopper occasionally, in order to hasten the change of the carbonate of lime. Now, without disturbing the precipitate, filter the clear fluid through a small plaited filter, which will take a very short time, throw the filter at once into the flask containing the precipitate and the rest of the fluid, and proceed according to II., *e*. This process has been in use for 10 years in my laboratory for all mineral water analyses; it is extremely simple, and gives excellent results.* If the water contains alkaline bicarbonate put a quantity of chloride of calcium sufficient to decompose the alkaline carbonate with the lime in the flask before adding the water.

β. WITH CHLORIDE OF BARIUM OR CHLORIDE OF CALCIUM AND AMMONIA.

Mix solution of chloride of barium or chloride of calcium† with excess of ammonia, boil for a short time, when a precipitate of carbonate of baryta or lime will usually fall, allow to deposit, and filter the clear fluid while still warm without delay, exposing to the air as little as possible. Transfer from 50 to 80 c.c. of this solution, freshly prepared, to a flask holding about 300 c.c., and close the latter with an india-rubber stopper. For adding the carbonic acid water one of the methods given in *a* is employed. If the water contains only free carbonic acid, the mixture remains clear at first, carbamate of ammonia $(NH_4O,C\left\{\begin{matrix}O\\ H_2N\end{matrix}\right.CO_2)$, being formed, but if it contains a carbonate also, a partial precipitation of carbonate of baryta or lime takes place immediately. As the carbamate of ammonia is but slowly converted by the action of water in the cold,‡ particularly in the presence of free ammonia,§ the fluid must be heated in order to precipitate all the carbonic acid in the form of alkaline earthy carbonate. From experiments of my own‖ I have come to the conclusion that the best way of applying heat is to place the flask in a tall vessel filled with water, keeping it down if necessary with a lead ring, and to boil the water. The contents of the flask will thus reach a temperature of 98°, and the precipitation will be complete in one and a half or two hours. A lower heat would require a much longer time, and active ebullition would occasion the loss of carbonate of ammonia in consequence of the action of chloride of ammonium upon alkaline earthy carbonate. Finally allow to cool and proceed according to one of the following methods:—

aa. Gravimetrically: Decant the supernatant fluid rapidly on to a filter, secluded as much as possible from access of air; fill the flask with water containing a few drops of ammonia free from carbonic acid, and insert the cork; shake, allow to deposit, decant again, and repeat this washing by decantation once more; transfer the precipitate now to the filter, wash until the last washings remain clear upon addition of solution of nitrate of silver, dry, ignite gently, and weigh (§ 101, 2, *a*). The amount of the carbonic acid may now be calculated from the weight of the carbonate of baryta, provided the analysed solution contained, besides carbonic acid, no other substance liable to be precipitated by ammonia and chloride of barium. But should this not be the case, and the precipitated carbonate of baryta contain an admixture of carbonate of lime, phosphate of baryta, sesquioxide of iron, or other such substances, the carbonic acid must be determined in the gently ignited, but not weighed precipitate, according to one of the methods given in II.; for instance, as directed in II., *c* (Fusion with borax glass). The filter, freed as completely as possible from adhering matter, should be incinerated, and the ash moistened with carbonate of ammonia, gently ignited and added to the precipitate. If the quantity of the precipitate is very large, it is best first to weigh the whole of it, and then to determine the carbonic acid in a weighed portion of the uniformly mixed powder.

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* Zeitschr. f. anal. Chem. 2, 49 and 341.

† The former should be used if you are going to conduct the subsequent process according to *aa*, the latter if you are going to proceed according to *bb*.

‡ Zeitschr. f. anal. Chem. 5, 321. § DIVERS, Journ. Chem. Soc. (2), 8, 359.

‖ Zeitschr. f. anal. Chem. 2, 60.

If the last particles of the precipitate cannot be removed from the flask by mechanical means, they are dissolved in a little dilute hydrochloric acid (the glass having previously been thoroughly washed), the solution is precipitated with carbonate of soda, and the trifling precipitate formed filtered off on a separate small filter, which is incinerated with the larger one.

bb. Volumetrically: Filter as in *aa*; there is no necessity, however, to collect the whole of the precipitate on the filter, as the last particles adhering to the inside of the flask may be left and washed by decantation. The washing with water containing a few drops of ammonia must be continued till the washings remain perfectly clear with silver solution. Put the funnel with the filter containing the precipitate on the flask in which the precipitation has been effected, pierce the point of the filter, and rinse the precipitate into the flask, with the aid of a washing bottle. Finally, spread the filter out on a glass plate and rinse the still adhering particles of the precipitate also into the flask—this can be done with ease. Since the precipitate, though perfectly washed, still retains small quantities of ammonia, in order to expel the same, heat the contents of the flask to gentle boiling for half an hour. Add now a little tincture of litmus, and then, from a MOHR's burette, normal (or, according to circumstances, decinormal) nitric or hydrochloric acid, until the fluid shows a distinct red color; expel the carbonic acid by heat, and then add standard solution of soda until the fluid just appears blue. After noting the number of c.c. of the acid and soda, add again about 1 c.c. of acid, and, after heating to boiling, solution of soda until the fluid again just appears blue. This operation may be repeated several times. By subtracting the volume of acid corresponding to the volume of solution of soda used in the process from the entire volume of acid added in each experiment, you find the quantity of acid which has served to expel from the carbonate of lime or baryta the carbonic acid, and is accordingly equivalent to the latter. For the details of this method, see § 223. As the coloring matter of the litmus is sometimes thrown down, along with silicic acid separating from the precipitate, it is occasionally found necessary to add again some tincture of litmus. If this should fail to lead to the desired result, solution of soda is added until the reaction is almost complete; the height of the soda solution left in the burette is then read off, the fluid diluted to a certain definite volume, and filtered; one-half the volume taken of the clear filtrate and solution of soda very cautiously added until the fluid appears blue; the quantity of soda solution required to effect this purpose is then doubled, and the result added to the quantity first used. As a matter of course, turmeric paper may be used here as in γ, instead of litmus, to determine the commencement of the alkaline reaction.

These methods given under β, only yield good results when the numerous sources of error are avoided with the greatest care. Usually the results obtained are too high, because the clear mixture of chloride of calcium and ammonia contains carbamate of ammonia, either from this substance not having been fully decomposed before filtering or from carbonic acid being taken up from the air on filtering, and in *bb*, more particularly, a falsely increased result will be obtained, if it is neglected to remove the ammonia adhering to the precipitate by long boiling or ignition. These circumstances which tend to raise the result are partially compensated by the fact that the alkaline earthy carbonates are not absolutely insoluble in the fluid containing chloride of ammonium and in the wash-water. Again, as already remarked, if the mixture of the carbonic acid water with chloride of calcium or chloride of barium and ammonia be not heated as directed the results will fall too low, either through the imperfect decomposition of the carbamate of ammonia by insufficient heating or through loss of carbonate of ammonia by active ebullition.

γ. AFTER PETTENKOFER.*

The principle of this simple and expeditious process consists in mixing the carbonic acid water with a measured quantity of standard lime water (or, under certain circumstances, baryta water) in excess. After complete separation of the carbonate of lime or baryta, the excess of alkaline earth in the fluid is determined in an aliquot part by means of standard solution of oxalic acid; the difference gives the lime precipitated by the carbonic acid, and consequently the amount of the latter present.

If a water contains only free carbonic acid, the analyst has only to bear in mind— if lime-water is employed—that the carbonate of lime formed is at first, as long as it remains amorphous, very perceptibly soluble in water, to which it communicates an alkaline reaction. Hence the unprecipitated lime in the fluid cannot be estimated till the carbonate of lime has separated in the crystalline form, which takes 8 or 10 hours, unless the mixture is warmed to 70° or 80°. On this account it is generally best to use baryta water (see "Analysis of Atmospheric Air").

If, on the contrary, a water contains an alkaline carbonate or any other alkaline salt whose acid would be precipitated by lime or baryta, a neutral solution of chloride of calcium or barium must first be added to decompose the same. This addition, too, prevents any inconvenience arising from the presence of free alkali in the lime or baryta water, or of carbonate of magnesia in the carbonic acid water; this inconvenience consists in the fact that oxalate of an alkali or of magnesia enters into double decomposition with carbonate of lime (which is seldom entirely absent from the fluid to be analysed), forming oxalate of lime and carbonate of the alkali or of magnesia, which latter will of course again take up oxalic acid.

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* BUCHNER'S neues Repert. 10, 1; Journ. f. prakt. Chem. 82, 32; Annal. d. Chem. u. Pharm. ii., Supplementb. 1; Zeitschr. f. anal. Chem. 1, 92.

In the presence of magnesia salts in the carbonic acid water, in order to avoid the precipitation of the magnesia, a little chloride of ammonium must also be added, but in this case heat must not be applied to induce the carbonate of lime to become more quickly crystalline, as ammonia would be thereby expelled.

In making the determination the first thing to be done is to ascertain the relation between the lime or baryta water and a standard solution of oxalic acid. PETTENKOFER makes the latter solution by dissolving 2·8636 grm. pure uneffloresced dry crystallized oxalic acid to 1 litre; 1 c.c. of this is equivalent to 1 mgrm. carbonic acid. The lime water is standardized as follows: measure 45 c.c. into a little flask which can be closed by the thumb, and then run in from the burette the solution of oxalic acid till the alkaline reaction has just vanished. During the operation the flask is closed with the thumb and gently shaken. The end is attained as soon as a drop taken out with a glass rod and applied to delicate turmeric paper* produces no brown ring. The first experiment is a rough one, the second should be exact.

The analysis of a carbonic acid water (a spring water, for instance) is performed by transferring 100 c.c. to a dry flask, adding 3 c.c. of a neutral and nearly saturated solution of chloride of calcium or barium, and 2 c.c. of a saturated solution of chloride of ammonium, then 45 c.c. of the standard lime or baryta water; close the flask with an india-rubber stopper, shake and allow to stand 12 hours. The fluid contents of the flask measure consequently 150 c.c. From the clear fluid† take out by means of a pipette two portions of 50 c.c. each, and determine the free lime or baryta by means of oxalic acid, in the first portion approximately, in the second exactly. Multiply the c.c. used in the last experiment by 3 and deduct the product from the c.c. of oxalic acid which correspond to 45 c.c of lime or baryta water. The difference shows the lime or baryta precipitated by carbonic acid, each c.c. corresponds to 1 mgrm. carbonic acid.

The method is convenient and good; it is especially to be recommended for dilute carbonic acid water. When sulphate or carbonate of lime is present, as is almost always the case in spring water, you must always before titrating await the conversion of the amorphous carbonate of lime to the crystalline state, even if baryta water is used (K. KNAPP‡). Baryta water therefore possesses no advantages over lime water for the analysis of spring waters.

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* For the preparation of this bibulous paper should be used, the ash of which is free from carbonate of lime. Swedish filtering-paper answers best. J. GOTTLIEB (Journ. f. prakt. Chem. 107, 488, Zeitschr. f. anal. Chem. 9. 251) prefers aqueous tincture of litmus, prepared from litmus first exhausted with spirit and used in a very dilute state. E. SCHULZE and M. MARCKER (Zeitschr. f. anal. Chem 9, 334) employ corallin or rosolic acid, which they say is specially adapted for the purpose. The alcoholic solution is cautiously neutralized with potash, and a drop or two of this tincture is added. F. SCHULZE (Zeitschr. f. anal. Chem. 9, 292) recommends spirituous tincture of turmeric.

† It is not admissible to use a filter (A. MÜLLER, Zeitschr. f. anal. Chem. 1, 84).

‡ Annal. d. Chem. u. Pharm. 158, 112; Zeitschr. f. anal. Chem. 10, 361.

II. *Separation of Carbonic Acid from the Bases, and its Estimation in Carbonates.*

a. Separation from Neutral Carbonates of Alkalies and the Alkaline Earths.

If the salts contain unquestionably 1 eq. carbonic acid to 1 eq. base, and there is no other salt with power to neutralize an acid present, we may determine the quantity of the base by the alkalimetric method (§§ 219, 220, 223), and calculate for each 1 eq. base 1 eq. carbonic acid.

b. Separation from Bases which upon ignition readily and completely yield their Carbonic Acid.

Such are, for instance, the carbonates of zinc, cadmium, lead, copper, magnesia, &c.

α. Anhydrous Carbonates.—Ignite the weighed substance, in a platinum crucible (carbonates of cadmium and lead in a porcelain crucible), until the weight of the residue remains constant. The results are, of course, very accurate. Substances liable to absorb oxygen upon ignition in the air are ignited in a bulb-tube, through which a stream of dry carbonic acid gas is conducted. The carbonic acid is inferred from the loss.

β. Hydrated Carbonates.—The substance is ignited in a bulb-tube through which dried air or, in presence of oxidizable substances, carbonic acid is transmitted, and which is connected with a chloride of calcium tube, by means of a dry, close-fitting cork. During the ignition, the posterior end of the bulb-tube is, by means of a small lamp, kept sufficiently hot to prevent the condensation of water in it, care being taken, however, to guard against burning the cork. The loss of weight of the tube gives the amount of the water + the carbonic acid; the increase of weight gained by the chloride of calcium tube gives the amount of the water, and the difference accordingly that of the carbonic acid. A somewhat wide glass tube may also be put in the place of the bulb-tube, and the substance introduced into it in a little boat, which is weighed before and after the operation.

c. Separation from all Bases, without exception, in Anhydrous Carbonates.

Fuse vitrified borax in a weighed platinum crucible, allow to cool in the desiccator, weigh, then transfer the well-dried substance to the crucible and weigh again. The weights of both carbonate and borax are thus ascertained. They should be in about the proportion of 1 : 4. Heat is then applied, which is gradually increased to redness, and maintained at this temperature until the contents of the crucible are in a state of calm fusion. The crucible is now allowed to cool, and weighed. The loss of weight is carbonic acid. The results are very accurate (SCHAFFGOTSCH).

I must add that borax-glass may be kept in a state of fusion at a red heat for $\frac{1}{4}$ to $\frac{1}{2}$ an hour without the occurrence of any volatilization, but that at a white heat (by igniting over the gas-bellows), even in a few minutes, it suffers a decided loss.* A few bubbles of carbonic acid remaining in the fusing mass are without any influence on the result.

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* Zeitschr. f. anal. Chem. 1, 65.

Instead of vitrified borax fused bichromate of potash may be used in the proportion of 5 to 1 of the carbonate (H. Rose*). The heat applied in this case must be low, and great caution must be used, or the bichromate will lose weight of itself.† The carbonic acid may be expelled from alkaline carbonates by strong ignition with ignited silica (H. Rose‡).

d. Separation from all Bases without exception. (Estimation of the Acid from the loss of weight.)

aa. Carbonates whose Bases form Soluble Salts with Sulphuric Acid.

The process is conducted in the apparatus illustrated by fig. 89.

The size of the flasks depends upon the capacity of the balance. *B* may be smaller than *A*. The tube *a* is closed at *b* with a little wax ball, or a small piece of india-rubber tube, stopped with half an inch of rod; the other end of the tube *a* is open, as are also both ends of *c* and *d*. The flask *B* is nearly half filled with concentrated sulphuric acid, free from oxides of nitrogen and sulphurous acid. The tubes must fit air-tight in the corks, and the latter equally so in the flasks. The weighed substance is put into *A*; this flask is then filled about one-third with water, the cork properly inserted, and the apparatus tared on the balance. A few bubbles of air are now sucked out of *d*, by means of an india-rubber tube. This serves to rarefy the air in *A* also, and causes the sulphuric acid in *B* to ascend in the tube *c*. The latter is watched for some time, to ascertain whether the column of sulphuric acid in it remains stationary, which is a proof that the apparatus is air-tight. Air is then again sucked out of *d*, which causes a portion of the sulphuric acid to flow over into *A*. The carbonate in the latter flask is decomposed by the sulphuric acid, and the liberated carbonic acid, completely dried in its passage through the sulphuric acid in *B*, escapes through *d*. When the evolution of the gas slackens a fresh portion of sulphuric acid is made to pass over into *A*, by renewed suction through *d*; the operation being repeated until the whole of the carbonate is decomposed. A more vigorous suction is now applied, to make a large amount of sulphuric acid pass over into *A*, whereby the contents of that flask are considerably heated; when the evolution of gas bubbles has completely ceased, the stopper on *a* is opened, and suction applied to *d*, until the air sucked out tastes no longer of carbonic acid.§ When the apparatus is quite cold it is replaced upon the balance, and the equilibrium

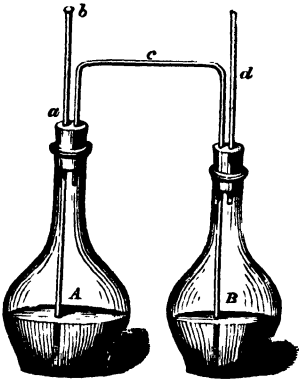

Fig. 89.

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* Pogg. Annal. 116, 131.

† Zeitschr. f. anal. Chem. 1, 183.

‡ Pogg. Annal. 116, 686.

§ In accurate experiments, it is advisable to connect the end *b* of the tube *a* with a chloride of calcium tube during the process of suction, and to use an aspirator or hydraulic air-pump instead of the mouth.

restored by additional weights. The sum of the weights so added indicates the amount of carbonic acid originally present in the substance.

If the flasks *A* and *B* are selected of small size, the apparatus may be so constructed that, together with the contents, it need not weigh above 70 grammes, admitting thus of being weighed on a delicate balance. The results obtained by the use of this apparatus, first suggested by WILL and myself, are very accurate, provided the quantity of the carbonic acid be not too trifling. Various modifications of the apparatus have been proposed, principally in order to make it lighter. Compare the note p. 340.

If sulphites or sulphides are present, together with the carbonates, their injurious influence is best obviated by adding to the carbonate solution of yellow chromate of potassa in more than sufficient quantity to effect their oxidation. If chlorides are present, in order to prevent the evolution of hydrochloric acid, add to the evolution flask a sufficient quantity of sulphate of silver in solution, or connect the exit tube *d* with a small prepared U-tube, which is, of course, first tared with the apparatus, and afterwards weighed with it. This U-tube is prepared—in accordance with the happy proposal of STOLBA—by filling with fragments of pumice which have been boiled with an excess of concentrated solution of sulphate of copper, till the air has been expelled, and then dried and heated to complete dehydration of the copper salt. If the U-tube is only 8 cm. high and has a bore of 1 cm., it answers the purpose very well. The outer end is provided with a perforated cork and short glass tube. We apply suction to this by means of a flexible tube, instead of to *d*.

bb. Carbonates whose Bases form Insoluble Salts with Sulphuric Acid.

The analysis of such carbonates cannot well be effected by the method *aa*, as the insoluble sulphate formed (sulphate of lime, for instance) partially protects the yet undecomposed portion of the carbonate from decomposition. The apparatus is therefore modified as shown in fig. 90.

The alteration consists simply in the tube *ab*, which contains a bulb, and is drawn out to a fine point at the lower end.

The process is conducted as follows: The weighed substance is put into *A*, together with water. The bulb-tube *ab* contains an amount of dilute nitric acid,* more than sufficient for the decomposition of the carbonate, which is prevented from flowing through the narrow aperture of the tube by the wax or india-rubber stopper at *b*. The point of this tube must not at first dip into the water in *A*. The apparatus having been tared on the balance, the tube *a* is carefully and cautiously moved down, until its point nearly touches the bottom of *A*. The stopper at *b* is then momentarily raised, so as to allow a small quantity of nitric acid to flow out; the operation being repeated until the carbonate is completely decomposed. The contents of *A* are then heated to incipient boiling, the stopper at *b* removed, and the carbonic acid sucked out of the apparatus as directed in *aa*. The loss of weight is ascertained when the apparatus has completely cooled.

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* In the presence of substances which decompose nitric acid, as for instance protoxide of iron, use hydrochloric acid of 10 per cent.

It will be seen at a glance that a different construction may also be given to the apparatus; that, for instance, the tube *C* may be connected, instead of with *B*, with a chloride of calcium tube, or with a tube filled with pumice stone or asbestos moistened with sulphuric acid; also, that the substance may be put into a small tube, which stands upright at first, or is suspended from a thread, but is subsequently, after taring the apparatus, upset or lowered into the dilute acid in the flask; also, that the closing of *a* may be effected by means of a clip, &c. Such modifications, if they are judicious, have very little or no influence on the accuracy of the results. Fig. 91 shows an apparatus modified in this manner by Fr. Mohr.

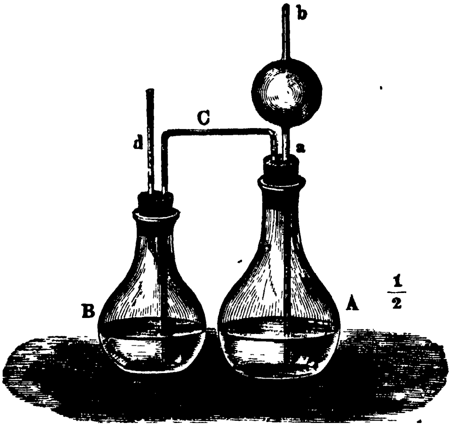

Fig. 90.

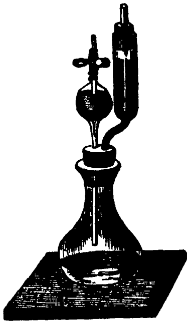

Fig. 91.

The apparatus proposed by Geissler[*] is one of the most convenient (fig. 92). It consists of two parts, *A B* and *C*. *C* is ground into the neck of *A* (*a*), so as to close air-tight, and yet admit of being readily removed, for the purpose of filling and emptying *A*. *b c* is open at both ends, and ground water-tight into *C*, at the lower end (*c*); it is kept in the proper position by means of an easily movable cork, *i*. The figure shows the construction of the apparatus in other respects. The cork *e* must fit air-tight, as must the tube *d* in the cork. The weighed substance is put into *A*, water added to the extent indicated, and the substance shaken towards the side of the flask. *C* is now filled nearly to the top with dilute nitric acid, or hydrochloric acid of 10 per cent.,

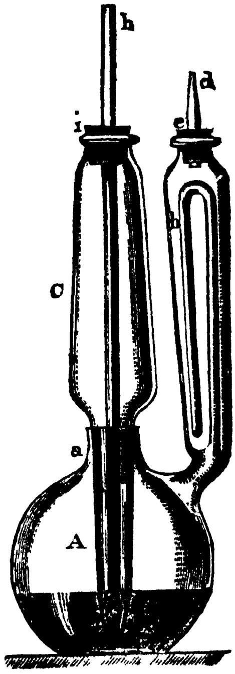

Fig. 92.

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[*] Journ. f. prakt. Chem. 60, 35.

with the aid of a pipette, after having previously turned the cork *i* upwards, without raising *b*; the cork is then again twisted down again, and *C* inserted into *A*; *B* is filled somewhat more than half with concentrated sulphuric acid, and *b* closed at the top with a little wax stopper, or a piece of india-rubber tube, with a small glass rod inserted in it. After taring the apparatus, the decomposition is effected by raising *b* a little, and thus causing acid to pass from *C* into *A*. The carbonic acid escapes through *h* into the sulphuric acid, where it is dried; it then leaves the apparatus through *d*. After the decomposition has been effected, *A* is cautiously heated to incipient boiling, the stopper on *b* opened, and the carbonic acid still remaining in the apparatus sucked out through *d*, by means of a small india-rubber tube. The apparatus is finally weighed when cold.[*]

If it is necessary to decompose the carbonate with hydrochloric acid. dry the escaping gas with pumice-stone saturated with anhydrous sulphate of copper which also retains hydrochloric acid as well as the moisture (Stolba[†]). It is well to fill a light U-tube with this material. The size of the U-tube should depend on the size of the apparatus. It can be used as long as a third of its contents remains uncolored.

It is often an advantage, for instance, in the case of pasty precipitates, to combine the estimation of the carbonic acid with that of the base according to II. *a*, by employing a measured quantity of standard acid for the decomposition. The point of the bulb-tube of the apparatus fig. 90, is closed with tallow, and the standard acid is then introduced into the bulb from a burette provided with a fine jet. The apparatus being weighed, the tallow is melted by a little heat

e. From all Bases without exception (Estimation of the Acid from the increase of weight of an Absorption Apparatus.)

This process, which was formerly but seldom employed, has been much recommended by Kolbe[§]. I have done my best—making free use of all that has been done by G. J. Mulder, Stolba, and Kolbe—to put this process into the most practical form possible, and I have now employed it for more than ten years, almost to the exclusion of all others There are few methods equal to it in accuracy.

The arrangement of the apparatus which I use at present is given in fig. 93.

A is the decomposing flask, it holds from 150 to 300 c.c., and is closed by a doubly-perforated caoutchouc stopper; *bb′* is a doubly-bent tube, expanded at *c* to a bulb, it may be connected at will, either with the funnel *e*, or with the soda-lime tube *f*, which again is connected on the other side with the flask *g*, containing potash. The tube *h* is ground below obliquely. The U-tube *i* has a height of 17 cm. and a bore of 16 mm.; it contains chloride of calcium in the bend only.* *k* and *l* are similar tubes; the first contains chloride of calcium, the second sulphate of copper on pumice (p. 338). The four smaller tubes have a height of 11 cm. and a bore of 12 mm.; *m* contains chloride of calcium, *n* and *o* are each filled—the first five-sixths with coarsely granulated soda-lime (about 20 grm.), and the last one-sixth with coarsely granulated chloride of calcium. *p* contains in the first limb chloride of calcium, in the other soda-lime. *i*, *k*, *l*, and *m* serve to free the carbonic acid from aqueous vapor and hydrochloric acid; *n* and *o* are weighed, their soda-lime takes up the carbonic acid, and their chloride of calcium prevents any evaporation of water from the latter, which is heated by the absorption; *p* guards *n* and *o* from any aqueous vapor, &c., which might penetrate from without. The corks of *n* and *o* are coated with sealing-wax. The other tubes are closed with caoutchouc stoppers, or corks coated with sealing-wax. The apparatus, once fitted up, lasts a long time; it is only requisite, before

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[*] Other carbonic acid apparatus have been proposed by H. Rose, Fritzsche, Rogers (see H Rose's Handbuch der analyt Chem. 6 Aufl. ii. 784); Vohl (Annal. d. Chem. u. Pharm. 66 247); M. Schaffner (Annal. d. Chem. u. Pharm. 82, 335); Werther (Modification of Geissler's apparatus—Journ. f. prakt. Chem. 61, 99); J. D. Smith (Chem. Gaz. 1855, 201); A. Mayer (Journ. f. prakt. Chem. 67, 63); Th. Simmler (Journ. f. prakt. Chem. 71, 158); Al Bauer (private communication); P. Hart (Chem. Gaz. 1859, 174); C. D. Braun (Dingler's polyt. Journ. 155, 301); E. J. Reynolds (Chem. News, 1862, 143); Stolba (Zeitschr. f. anal. Chem. 1, 368); Ullgren (*Ib.* 8, 46); Johnson (*Ib* 9, 90); Bunsen (*Ib.* 10, 403) and others. Johnson fills the apparatus and saturates the acid with carbonic acid before commencing, and therefore does not remove the carbonic acid from the apparatus at the end. It need hardly be mentioned that in this case the atmospheric pressure and temperature must be the same during both weighings.

[†] Dingler's polyt. Journ. 164, 128.

[‡] Journ. f. prakt. Chem. 97, 312; Zeitschr. f. anal. Chem. 5, 208 and 6, 444.

[§] Annal. d. Chem. u. Pharm. 119, 130.

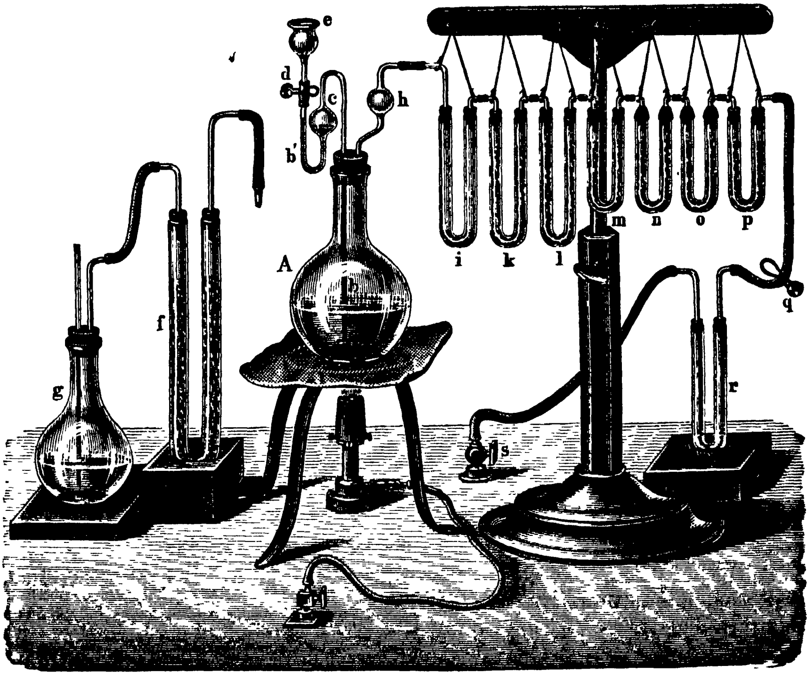

Fig. 93.

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* All the chloride of calcium used in this apparatus should be entirely free from alkaline reaction. To prevent any alkalinity it is well to add a little chloride of ammonium to the solution before evaporating.

each experiment, to renew the chloride of calcium in *i*, and to refill *n*, and occasionally *o*.

Having weighed the substance, transferred it to *A*, and added a little water, weigh *n* and *o*, connect the various parts of the apparatus, join *b* and *e*, close *d*, and apply suction by means of the hydraulic air-pump or an aspirator to the end of the flexible tube *s*, which is in conjunction with the U-tube *r*, containing a little water, and also with *p*. The clip *q* is in the meantime opened. The passing of gas bubbles through the water in *r* will soon cease if the apparatus is quite air tight. Fill *e* with dilute hydrochloric acid (or occasionally nitric acid), and opening *d* with care allow a little to enter *A*. The evolution of carbonic acid will immediately commence, and its rate may be noted by the passage of the air bubbles through the water in *r*. When the evolution begins to slacken open *d*, and run a little more hydrochloric acid into *A*. If the amount of hydrochloric acid has been properly adjusted, the decomposition of the carbonate will be complete when the last of the hydrochloric acid has run from *e* into *A*. Now pass a little water through *d* to rinse *e* into *A*; remove *e*, connect *f* with *d*, and opening *d* cautiously draw a gentle current of air continuously through the apparatus, heating the contents of *A* to incipient ebullition.

As soon as the carbonic acid gets to the soda-lime tubes, they become heated, and this progressive heating affords a good measure of the extent to which the soda-lime is saturated with carbonic acid. When the soda-lime tubes are quite cool, the principal quantity of the carbonic acid will have been absorbed, and if the air is passed for five or ten minutes longer, you may be certain that all the carbonic acid is removed from *A*, *i*, *k*, *l*, and *m*. But little water will arrive at *i* if the heating of *A* has been properly managed, and the chloride of calcium will not be quite deliquesced.

When the experiment is finished, stop the suction at *s*, remove the tubes *n* and *o*, and weigh them. The increase in their weight expresses the amount of carbonic acid in the substance. The results are so concordant and exact that they leave nothing to wish.* The bases are free from any impurity and completely dissolved in hydrochloric (or nitric) acid.

For a second experiment charge *i* and *n* afresh. *o* need not be refilled as a rule, but it is well to transpose it and *n*.

If it is preferred to decompose the carbonate in the dry way, this may be done by fusing the finely pulverized salt (alkaline carbonates need not be in a fine state of division) with six or nine times its amount of fused bichromate of potash. In the fusion a piece of combustion tube is used, slightly bent at the middle, to hold the mixture; it is connected on one side with the apparatus for purifying the air, on the other side with a chloride of calcium tube for drying the carbonic acid, soda-lime tubes for absorption, a guard tube, and an aspirator or hydraulic air-pump. A gentle current of air being established, the combustion tube is heated, and the heat is removed, when the mass fuses calmly. The current of air is kept up a little longer, and then the absorption tubes are weighed. The method does not require any modification in the presence of sulphides, sulphites, or hyposulphites (PERSOZ*).

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* Zeitschr. f. anal. Chem. 2, 49 and 341.

f. Separation from all Bases without exception (Estimation of the Acid by Expulsion, Absorption, and Volumetric Analysis).

If the carbonic acid be disengaged in the evolution apparatus mentioned in *e* (which I consider the most suitable form), or in a similar one, we may, of course, determine the gas according to the methods given above for the estimation of free carbonic acid; that is, we may collect it in a mixture of chloride of barium or chloride of calcium and ammonia, proceed as directed I., *b* β., finishing the analysis according to *bb*. But this method is far more troublesome and slow than that detailed in *e*, and cannot be relied upon unless all the sources of error already pointed out are avoided.

On the contrary, it is sometimes advantageous, especially in the estimation of very small quantities of carbonic acid, to receive the same in a known volume of standard baryta-water, and to complete the analysis according to PETTENKOFER's principle (I., *b*, γ). As this method finds application in the analysis of air, I refer to this section, merely remarking that AL. MULLER,† E. SCHULZE,‡ and P. WAGNER§ have given special apparatus and rules for conducting the process in a most satisfactory manner.

g. Estimation by Measuring the Gas.

a. After C. SCHEIBLER.‖ This process is applicable in the case of all salts which are decomposed by hydrochloric acid in the cold. It is distinguished for rapid and convenient execution and very satisfactory results, but it requires a special apparatus. It is much employed to determine the carbonate of lime in bone-earth.

The ingenious apparatus employed is represented by fig. 94. *A* contains the carbonate to be decomposed. The decomposition is effected by raising the bottle, as shown, and thus causing the hydrochloric acid in the gutta-percha tube *S* to run out. The glass stopper to *A* is well ground, and also greased; it is perforated through the middle and a short glass tube is cemented into the opening. The liberated carbonic acid passes through this, the india-rubber tube *r* and a glass tube cemented into one of the perforations of the stopper of the bottle *B*, and finally enters the bladder *K*, which is made of caoutchouc of the thickness of letter paper, and is connected air-tight with the glass tube communicating with *A*. Another hole in the stopper of *B* is closed with a clip and the middle hole is connected with the glass tube *v*. The latter leads to the measuring apparatus. This consists of the graduated glass tube *C*, of 150 c.c. capacity, and divided into ½ c.c.; it is connected, as shown in the figure, with the equally wide plain tube *D*. In the caoutchouc stopper at the lower end of the latter there is a second short glass tube, this is connected by means of the india-rubber tube closed by *P*, with a glass tube, which is cemented into the bottle *E*, and reaches nearly to the bottom. A short glass tube bearing the

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[*] Compt. rend. 58, 239; Zeitschr. f. anal. Chem. 1, 83.

[†] Zeitschr. f. anal. Chem. 1, 47. [‡] *Ib.* 9, 290. [§] *Ib.* 9, 445.

[‖] Anleitung zum Gebrauch des Apparates zur Bestimmung des kohlensauren Kalkerde in der Knochenkohle, &c., von Dr. C. SCHEIBLER. Printed in manuscript, Berlin, 1862.

flexible tube *v* is cemented into the second tubulure of the bottle *E*. This bottle is the reservoir of water; if *P* is opened the water contained in the tubes *D* and *C* flows into *E*; if you now blow into *v*, *P* being still open, the water in *E* rises into the tubes. *E* is in the beginning nearly filled with distilled water through *D*.

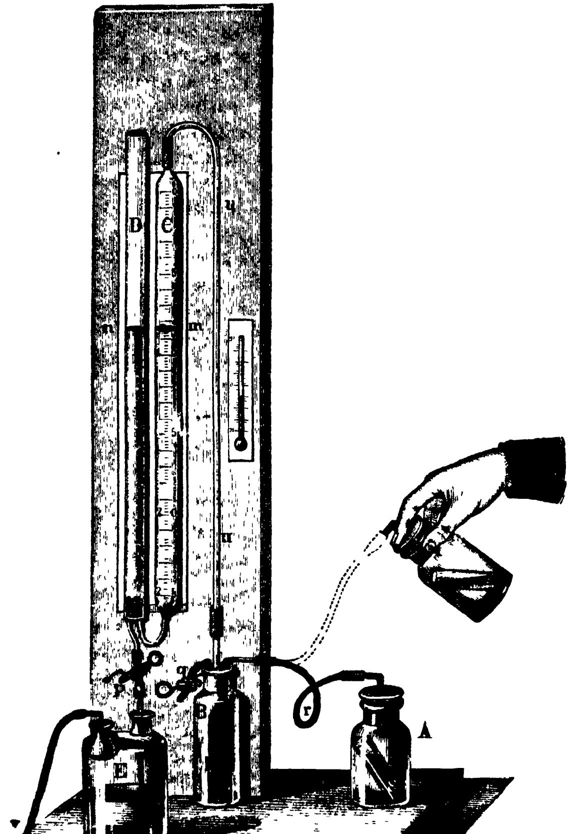

Fig. 94.

All the parts of the apparatus, with the exception of the decomposing bottle *A*, remain permanently connected; it is therefore advisable to fix them to the wooden stand by metal fastenings. The stand should also carry a thermometer.

Each experiment is commenced by filling the tubes *C* and *D* to zero with water. This is done by blowing in at *v*, the stopper of *A* being removed. As soon as the column of water stands a little above zero, close *P*, and then slightly opening it again, allow water to drop out till the object is attained. It is hardly necessary to mention that the blowing air into *v* and the handling of the clip require caution, for if the water were to pass through *u* into *B*, the whole apparatus would have to be taken to pieces and the water removed. While the tube *C* is filling with water, the expelled air passes into *B*, and compresses the caoutchouc bladder. If this does not take place to a sufficient extent, blow cautiously into *B* at *q*, till the bladder is completely collapsed. In experiments that follow one upon another, the bladder always empties itself. Should it happen that the bladder is on any occasion empty, before the water in the tubes has reached zero, then the water in the tubes would not stand in equilibrium. In such case open *q* for a moment. The experiment should be made in a room in which the temperature is as constant as possible, and care should be taken that the apparatus is not exposed to the direct action of the sun, or the radiant heat of a stove, for sudden changes of temperature during the experiment would of course interfere with its accuracy.

Put the very finely powdered substance into the perfectly dry decomposing glass *A*, fill the gutta-percha tube with 10 c.c. hydrochloric acid of 1·12 sp. gr., place the tube cautiously in the decomposing glass, and then close the bottle with the well-tallowed stopper. Here the water will sink a little in *C* and rise in *D*; open *q* for a moment, and the equilibrium will be restored. Now note the thermometer and barometer, hold the bottle with the right hand round the neck to avoid warming, raise it, incline it slightly so that the hydrochloric acid may mix with the substance gradually, and at the same time with the left hand regulate *P*, so that the water in the two tubes may be kept at exactly the same height; continue these operations without intermission till the level of the water in *C* does not change for a few seconds. Now bring the columns in *C* and *D* to exactly the same height, read off the height of the water and note whether the temperature has remained constant. If it has, the number of c.c. read off indicates the liberated carbonic acid; but as a small quantity has been dissolved by the hydrochloric acid, it is necessary to make a correction. SCHEIBLER has determined the small amount of carbonic acid which remains dissolved in the 10 c.c. hydrochloric acid at the mean temperature, and he directs to add 3·2 c.c. to the volume of the carbonic acid read off. Lastly, this volume is reduced to 0°, 760 mm. and the dry condition (comp. § 198).* 1000 c.c. of carbonic acid at the normal temperature and pressure weigh 1·97146 grm.

If you want to dispense with all corrections, you may begin each set of experiments by establishing the relation between the carbonic acid obtained in the process (*i.e.*, the CO_2 actually yielded + 3·2 c.c.) and pure carbonate of lime (a weighed quantity of finely pulverized and dried Iceland spar). This relation is of course dependent on the temperature and pressure prevailing on the particular day. Let us take an example. From ·2737 grm. carbonate of lime, containing ·120428 grm. carbonic acid, were obtained 63·8 c.c. (including the 3·2 c.c.), and in an analysis of dolomite, under the same circumstances, from ·2371 substance were obtained 57·3 c.c. (including the 3·2 c.c.).

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* This mode of correction involves some uncertainty, as the amount of carbonic acid remaining absorbed depends on the concentration of the saline solution obtained, the quantity of air with which the carbonic acid is mixed, and the whole quantity of carbonic acid evolved. Compare SCHEIBLER's later directions and DIETRICH, Zeitschr. f. anal. Chem. 3, 165.

Now 63·8 : 57·3 :: ·120428 : x—x = ·10816. Therefore ·2371 grm. substance contains ·10816 CO_2, therefore the dolomite contains 45·62 per cent. of carbonic acid. But this method of working cannot be expected to give correct results unless the saline solutions formed and the amounts of carbonic acid evolved are tolerably alike in the first experiment and in the analyses.

β. E. Dietrich* has devised a very convenient apparatus in which the evolved carbonic acid is measured over mercury; he also gives tables showing the weight of a c.c. of carbonic acid for pressures between 720 and 760 mm. and temperatures between 10° and 25°, and the amount of carbonic acid absorbed by 5 c.c. hydrochloric acid of 1·125 sp. gr. for evolved quantities between 1 and 100 c.c. of gas. With the aid of this apparatus and these tables we may make estimations of carbonic acid with great rapidity and exactness, so that the method is particularly to be recommended for long series of experiments.

γ. G. Rumpf† describes a very simple apparatus which may be put together in the laboratory. However this method affords no advantage unless you have Rumpf's tables, and as I have no room for these I must refer to the original memoir.

δ. To determine small quantities of carbonic acid in minerals you may proceed as follows. Procure a graduated tube provided with a glass cock, grease the latter, and connecting it with an air-pump fill it with mercury. Fold the mineral in blotting paper and pass it up the tube, send up a measured quantity of hydrochloric acid by means of a pipette whose point is bent upwards, and then measure the evolved gas. Of course you must take account of the gas absorbed by the hydrochloric acid. For the method of calculating the weight from the volume see § 198.

§ 140.

2. Silicic Acid.

I. *Determination.*

The direct estimation of silicic acid is almost invariably effected by converting the soluble modification of the acid into the insoluble modification, by evaporating and completely drying; the insoluble modification is then, after removal of all foreign matter, ignited strongly (over the bellows blowpipe) and weighed.

For the guidance of the student I would observe here that, to guard against mistakes, he should always *test the purity of the weighed silicic acid.* The methods of testing will be found below.

If you have free silicic acid in the state of hydrate, in an aqueous or acid solution free from other fixed bodies, simply evaporate the solution in a platinum dish, ignite and weigh the residue.

Respecting a volumetric estimation of silicic acid (conversion into silicofluoride of potassium and acidimetric determination of the same, see § 97, 5), I must refer to Stolba.‡

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* Zeitschr. f. anal. Chem. 3, 162; 4, 141, and 5, 49.

† *Ib.* 6, 398.

‡ *Ib.* 4, 163.

II. *Separation of Silicic Acid from the Bases.*

a. In all Compounds which are decomposed by Hydrochloric or Nitric Acid, on digestion in open vessels.

To this class belong the silicates soluble in water, as well as many of the insoluble silicates, as, for instance, nearly all zeolites. Several minerals not decomposable of themselves by acids, become so by persistent ignition in a state of fine powder (F. MOHR*). If the ignition is too strong particles of alkali may be lost.

The substance is very finely powdered,† dried at 100°, and put into a platinum or porcelain dish (in the case of silicates whose solution might be attended with disengagement of chlorine, platinum cannot be used); a little water is then added, and the powder mixed to a uniform paste. Moderately concentrated hydrochloric acid, or—if the substance contains lead or silver—nitric acid, is now added, and the mixture digested at a very gentle heat, with constant stirring, until the substance is completely decomposed, in other terms until the glass rod, which is rounded at the end, encounters no more gritty powder, and the stirring proceeds smoothly without the least grating.

The silicates of this class do not all comport themselves in the same manner in this process, but show some differences; thus most of them form a bulky gelatinous mass, whilst in the case of others the silicic acid separates as a light pulverulent precipitate; again, many of them are decomposed readily and rapidly, whilst others require protracted digestion. When the decomposition is effected, the mixture is evaporated to dryness on the water-bath, and the residue heated, with frequent stirring, until all the small lumps have crumbled to pieces, and the whole mass is thoroughly dry, and until no more acid fumes escape. It is always the *safest* way to conduct the drying on the water-bath. Occasionally it is well to moisten the dry mass with water and evaporate again. In cases where it appears desirable to accelerate the desiccation by the application of a stronger heat, an air-bath may be had recourse to; which may be constructed in a simple way, by suspending the dish containing the substance, with the aid of wire, in a somewhat larger dish of silver or iron, in a manner to leave everywhere between the two dishes a small space of uniform width. Direct heating over the lamp is not advisable, as in the most strongly heated parts the silicic acid is liable to unite again with the separated bases to compounds which are not decomposed, or only imperfectly, by hydrochloric acid.

When the mass is cold, it is brought to a state of semi-fluidity by thoroughly moistening it with hydrochloric acid; after which it is allowed to stand for half an hour, then warmed on a water-bath, diluted with hot water, stirred, allowed to deposit, and the fluid decanted on to a filter; the residuary silicic acid is again stirred with hydrochloric acid, warmed, diluted, and the fluid once more decanted; after a third repetition of the same operation, the precipitate also is transferred to the filter, thoroughly washed with hot water, well dried, and ignited at last as strongly as possible, as directed in § 52 or in § 53. For the properties of the residue, see § 93, 9. The results are accurate. The bases, which are in the filtrate as chlorides, are determined by the methods given above. Deviations from the instructions here given are likely to entail loss of substance; thus, for instance, if the mass is not thoroughly dried, a not inconsiderable portion of the silicic acid passes into the solution, whereas, if the instructions are strictly complied with, only traces of the acid are dissolved; in accurate analyses, however, even such minute traces must not be neglected, but should be separated from the bases precipitated from the solution. The separation may as a rule be readily effected by dissolving them, after ignition and weighing, in hydrochloric or sulphuric acid, by long digestion in the heat, the traces of silicic acid being left undissolved. Sometimes it is better to fuse the metallic oxides with bisulphate of potash, or to reduce them to the metallic state by ignition in hydrogen, and then to treat with hydrochloric acid. Again, if the silicic acid is not thoroughly dried previous to ignition, the aqueous vapor disengaged upon the rapid application of a strong heat may carry away particles of the light and loose silica. However, if a suction apparatus has been used, and the water has been removed as far as the apparatus will remove it, the precipitate may be ignited at once by the method given p. 85. But in this case the filter cannot usually be completely incinerated.

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* Zeitschr. f. anal. Chem. 7, 293.

† Very hard silicates cannot be powdered in an agate mortar without taking up silica; these must, therefore, be powdered in a steel mortar, sifted, and freed from particles of steel with the magnet.

The silicic acid may be tested as follows. This testing must on no account be omitted if the silica has been separated in a pulverulent and not in a gelatinous form. Heat a portion on a water-bath with moderately concentrated solution of carbonate of soda for an hour in a platinum or silver dish; with less advantage in a porcelain dish. EGGERTZ* recommends for ·1 grm. silicic acid 6 c.c. of a saturated solution of carbonate of soda and 12 c.c. of water. Pure silica would dissolve. If a residue remains, pour off the clear fluid and heat again with a small quantity of carbonate of soda. If a residue still remains, weigh the rest of the impure silica and treat it according to *b*, to estimate the amount of impurity.

If you have *pure* hydrofluoric acid, you may also test the silicic acid in a very easy manner, by treating it with this acid and some sulphuric acid in a platinum dish; upon the evaporation of the solution, the silicic acid, if pure, will volatilize completely (as fluoride of silicon). If a residue remains, moisten this once more with hydrofluoric acid, add a few drops of sulphuric acid, evaporate, and ignite; the residue consists of the sulphates of the bases which were mixed with the silicic acid, as well as any titanic acid that was present (BERZELIUS). Fluoride of ammonium may be used instead of hydrofluoric acid.

b. Compounds which are not decomposed by Hydrochloric or Nitric Acid, on digestion in open vessels.

a. Decomposition by Fusion with Alkaline Carbonate.

Reduce the substance to an impalpable powder, by trituration and, if necessary, sifting (§ 25); transfer to a platinum crucible, and mix with about 4 times the weight of pure anhydrous carbonate of soda or carbonate of soda and potassa, with the aid of a rounded glass rod; wipe the rod against a small portion of carbonate of soda on a card, and transfer this also from the card to the crucible. Cover the latter well, and heat, according to size, over a gas- or spirit-lamp with double draught, or a blast gas-lamp; or insert in a Hessian crucible, compactly filled up with calcined magnesia, and heat in a charcoal fire. Apply at first a moderate heat for some time to make the mass simply agglutinate; the carbonic acid will, in that case, escape from the porous mass with ease and unattended with spirting. Increase the heat afterwards, finally to a very high degree, and terminate the operation only when the mass appears in a state of calm fusion, and gives no more bubbles.

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* Zeitschr. f. anal. Chem. 7, 502.

The platinum crucible in which the fusion is conducted must not be too small; in fact, the mixture should only half fill it. The larger the crucible, the less risk of loss of substance. As it is of importance to watch the progress of the operation, the lid must be easily removable; a concave cover, simply lying on the top, is therefore preferable to an overlapping lid. If the process is conducted over the spirit- or simple gas-lamp, the mixed carbonates of soda and potassa are preferable to carbonate of soda, as they fuse much more readily than the latter. In heating over a lamp, the crucible should always be supported on a triangle of platinum wire, with the opening just sufficiently wide to allow the crucible to drop into it fully one-third, yet to retain it firmly, even with the wire at an intense red heat. When conducting the process over a spirit-lamp with double draught, or over a simple gas-lamp, it is also advisable, towards the end of the operation, when the heat is to be raised to the highest degree, to put a chimney over the crucible, with the lower border resting on the ends of the iron triangle which supports the platinum triangle; this chimney should be about 12 or 14 cm. high, and the upper opening measure about 4 cm. in diameter. The little clay chimneys recommended by O. L. ERDMANN are still more serviceable (fig. 20, p. 22, "Qual. Anal.") When the fusion is ended, the red-hot crucible is removed with tongs, and placed on a cold, thick, clean, iron plate, on which it will rapidly cool; it is then generally easy to detach the fused cake in one piece.

The cake (or the crucible with its contents) is put into a beaker, from 10 to 15 times the quantity of water poured over it, and heat applied for half an hour, then hydrochloric acid is gradually added, or, under certain circumstances, nitric acid; the beaker is kept covered with a glass plate, or, which is much better, with a large watch-glass or porcelain dish, perfectly clean outside, to prevent the loss of the drops of fluid which the escaping carbonic acid carries along with it; the drops thus intercepted by the cover are afterwards rinsed into the beaker. The crucible is also rinsed with water mixed with dilute acid, and the solution obtained added to the fluid in the beaker.

The solution is promoted by the application of a gentle heat, which is continued for some time after this is effected to insure the complete expulsion of the carbonic acid; since otherwise some loss of substance might be incurred, in the subsequent process of evaporation, by spirting caused by the escape of that gas. If in the process of treating the fused mass with hydrochloric acid, a saline powder subsides (chloride of sodium or chloride of potassium), this is a sign that more water is required.

If the decomposition of the mineral has succeeded to the full extent, the hydrochloric acid solution is either perfectly clear, or light flakes of silicic acid only float in it. But if a heavy powder subsides, which feels gritty under the glass rod, this consists of undecomposed mineral. The cause of such imperfect decomposition is generally to be ascribed to imperfect pulverization. In such cases the undecomposed portion may be fused once more with carbonated alkali; the better way, however, is to repeat the process with a fresh portion of mineral more finely pulverized.

The hydrochloric or nitric acid solution obtained is poured, together with the precipitate of silicic acid, which is usually floating in it, into a porcelain or, better, into a platinum dish, and treated as directed in II., *a*. That the fluid may not be too much diluted, the beaker should be rinsed only once, or not at all, and the few remaining drops of solution dried in it; the trifling residue thus obtained is treated in the same way as the residue left in the evaporating basin. This is the method most commonly employed to effect the decomposition of silicates that are undecomposable by acids; that it cannot be used to determine alkalies in silicates is self-evident.

β. Decomposition by means of Hydrofluoric Acid.

aa. By Aqueous Hydrofluoric Acid.

The silicate should be finely pulverized, dried at 100°, and occasionally ignited.* It is mixed, in a platinum dish, with rather concentrated, slightly fuming hydrofluoric acid, the acid being added gradually, and the mixture stirred with a thick platinum wire. The mixture, which has the consistence of a thin paste, is digested some time on a water-bath at a gentle heat, and pure concentrated sulphuric acid, diluted with an equal quantity of water, is then added, drop by drop, in more than sufficient quantity to convert all the bases present into sulphates. The mixture is now evaporated on the water-bath, during which operation fluoride of silicon gas and hydrofluoric acid gas are continually volatilizing; then it is finally exposed to a stronger heat at some height above the lamp, until the excess of sulphuric acid is almost completely expelled. The mass, when cold, is thoroughly moistened with concentrated hydrochloric acid, and allowed to stand at rest for one hour; water is then added, and a gentle heat applied. If the decomposition has fully succeeded, the whole must dissolve to a clear fluid. If an undissolved residue is left, the mixture is heated for some time on the water-bath, then allowed to deposit, the clear supernatant fluid decanted as far as practicable, the residue dried, and then treated again with hydrofluoric acid and sulphuric acid, and, lastly, with hydrochloric acid, which will now effect complete solution, provided the analysed substance was very finely pulverized, and free from baryta, strontia (and lead). The solution is added to the first. The bases in the solution (which contains them as sulphates, and contains also free hydrochloric acid), are determined by the methods which will be found in Section V.

This method, which is certainly one of the best to effect the decomposition of silicates, was proposed by BERZELIUS. It has been but little used hitherto, because we did not know how to prepare hydrofluoric acid, except with the aid of a distilling apparatus of platinum, or, at least, with a platinum head; nor to keep it, except in platinum vessels. These difficulties can now be considered as overcome, comp. § 58, 2. Never omit testing the acid before using it.

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* Many minerals are much more readily decomposed by hydrofluoric acid also, if they are previously ignited in a state of fine division (HERMANN, RAMMELSBERG, FR. MOHR, Zeitschr. f. anal. Chem. 7, 291).

The hydrofluoric acid may also be employed in combination with hydrochloric acid; thus 1 grm. of finely elutriated felspar, mixed with 40 c.c. water, 7 c.c. hydrochloric acid of 25% and 3½ c.c.hydrofluoric acid, and heated to near the boiling point, dissolves completely in three minutes. 4 c.c. sulphuric acid are then added, the sulphate of baryta which separates is filtered off, and the filtrate evaporated till no more hydrofluoric acid escapes (AL. MITSCHERLICH[*]).

The execution of the method requires the greatest possible care, both the liquid and the gaseous hydrofluoric acid being most injurious substances. The treatment of the silicate with the acid and the evaporation must be conducted in the open air, otherwise the windows and all glass apparatus will be attacked. As the silicic acid is in this method simply inferred from the loss,[†] a combination with method *a* is often resorted to.

bb. By Hydrofluoric Acid Gas.

Instead of the hydrofluoric acid dissolved in water, the gaseous acid also may be used to effect the decomposition of silicates. BRUNNER[‡] is the author of this method, which is very often employed. The process is as follows:—Put from 1 to 2 grm. of the silicate, very finely pulverized, in the thinnest possible layer, into a shallow platinum dish, and moisten the powder with dilute sulphuric acid; place the dish, supported on a leaden tripod or leaden ring, in the centre of a leaden box, which may have a diameter of 6 inches and a height of 6 inches, and on the bottom of which you have just before made a layer of about half an inch of powdered fluor-spar into a paste with concentrated sulphuric acid: in this latter operation, be cautious to avoid the escaping vapors; the mixing of the powdered fluor-spar with the sulphuric acid is effected with a long glass rod, or, better still, with a long leaden rod. As soon as you have placed the dish in the box, with the aid of pincers or tongs, put on the tightly fitting leaden cover, lute the joinings with plaster of Paris, and put the box in a warm place for from 6 to 8 days. If you wish to accelerate the process, you must not lute the joinings quite air-tight, and must heat the apparatus in the *open air*[§] by means of a small gas- or spirit-lamp; in this manner you may succeed in a few hours in effecting the decomposition of from 1 to 2 grm. of the powdered silicate, provided it is spread in a very thin layer, or stirred from time to time, which latter operation, however, requires caution.

If the decomposition has succeeded well, the residue in the platinum dish consists of silicofluorides and sulphates. Put the shallow dish now into a larger platinum dish, add, drop by drop, pure sulphuric acid, in somewhat more than sufficient quantity to effect the conversion of the bases into sulphates; evaporate in the air-bath, expel finally the excess of hydrated sulphuric acid over the lamp, almost, but not entirely, and treat the residue with hydrochloric acid and water in the manner directed in *aa*. The decomposition can only be considered complete if the residue entirely dissolves (of course, in presence of barium, you would expect to find a little sulphate of barium).

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[*] Journ. f. prakt. Chem. 81, 108.

[†] The silicon escaping in the form of fluoride may sometimes be determined directly, by the method of STORY MASKELYNE (Zeitschr. f. anal. Chem. 9, 380), which, however, requires a platinum retort of peculiar construction.

[‡] Pogg. Annal. 44, 134.

[§] An apparatus which may be used in the laboratory has been described by A. MÜLLER (Journ. f. prakt. Chem. 95, 51).

If you have a platinum tube adapted to the purpose, you may heat the powdered substance in a platinum boat inside the tube in a current of dry hydrochloric acid gas. The platinum tube is bent downwards in front and dips in water. The water takes up the volatile fluorides, the non-volatile ones remaining in the boat (SAINT-CLAIRE DEVILLE, KUHLMANN*).

cc. By Fluoride of Ammonium.

Mix the very finely powdered substance in a platinum dish with four times its weight of fluoride of ammonium, moisten well with concentrated sulphuric acid, heat on the water-bath till the evolution of fluoride of silicon and hydrofluoric acid slackens, add more sulphuric acid, heat again, finally somewhat more strongly till the greater part of the sulphuric acid has escaped, and treat the residue according to *aa* (L. v. BABO, J. POTYKA, R. HOFFMANN†). H. ROSE‡ first warms the silicate gently with seven times its amount of the fluoride and some water, then heats gradually to redness till no more fumes escape, and finally treats with sulphuric acid.

dd. By Fluoride of Hydrogen and Potassium, &c.

In silicates, which more or less resist the action of hydrofluoric acid, such as zircon and beryll, the bases with the exception of the alkalies may be determined by fusing with fluoride of hydrogen and potassium (MARIGNAC, GIBBS§), or by mixing with three parts of fluoride of sodium, adding 12 parts of bisulphate of potash to the crucible, and then heating at first very gently, afterwards more strongly till the mass fuses calmly. The residue is dissolved in water or hydrochloric acid (CLARKE‖).

γ. Decomposition by fusion with Hydrate of Baryta or Carbonate of Baryta.

The fusion of silicates with carbonate of baryta requires a very high degree of heat, attainable only by means of a good blast gas-lamp, a SEFSTRÖM furnace, a DEVILLE turpentine lamp, &c.; as the highest temperature attainable by means of a wind furnace does not cause agglutination of the carbonate of baryta and the silicate, without which complete decomposition cannot occur. But then, on the other hand, the action of carbonate of baryta is so energetic, that even the most refractory siliceous minerals are readily and completely decomposed by it. The proportion to be used is from 4 to 6 parts of carbonate of baryta to 1 part of the mineral. The fusion is effected in a platinum crucible, which, if a SEFSTRÖM furnace is used, is inserted in another crucible of refractory fire-clay, filled with magnesia. The crucible is left in the fire half an hour at least. The larger the amount of carbonate of baryta used the greater is the danger of volatilization of alkali. DEVILLE, in fact, recommends 8 parts of carbonate of baryta for 1 part of a felspathic mineral.

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* Compt. rend. 58, 545.

† Zeitschr. f. anal. Chem. 6, 366.

‡ Pogg. Annal. 108, 20.

§ Zeitschr. f. anal. Chem. 3, 399.

‖ *Ib.* 7, 463.

With more readily decomposable minerals, the object in view may be attained more easily with hydrate of baryta freed from its water of crystallization. From 4 to 5 parts of the hydrate are intimately mixed with 1 part of the mineral; it is advisable to cover the mixture with a layer of carbonate of baryta. The fusion may be effected over a common gas- or BERZELIUS spirit-lamp; silver crucibles are preferable to platinum, as the latter are slightly attacked in the operation. The mixture either fuses completely, or, at least, its particles agglutinate into a semi-fused mass. In order to be able to employ platinum crucibles V. FELLENBERG–RIVIER* recommends fusing 4 or 5 parts of chloride of calcium in the platinum crucible, shaking the crucible round while it is cooling, then adding 1 part of hydrate of baryta and fusing this. When the crucible is cold add about 1 part of the finely powdered substance, heat gently, and when no more evolution of gas takes place heat more strongly. SMITH† recommends with the same view fusing 2 parts of chloride of barium with 3 or 4 parts of carbonate of baryta and 1 part of the silicate.

When the operation is terminated—no matter whether carbonate or hydrate of baryta has been employed—the crucible is allowed to cool, carefully cleaned outside, and put with its contents into a beaker, where it is then covered with 10 or 15 parts of water, and allowed to soak for some time; hydrochloric or nitric acid is added, and the rest of the operation conducted as in *b*, *a*. Care must be taken, however, not to add too much hydrochloric acid at once, as the chloride of barium formed is difficultly soluble in that acid, and would consequently tend to impede further solution, by forming a kind of insoluble protecting crust round the still undissolved portion. In the solution filtered from the silicic acid, the bases are determined by the methods which will be found in Section V. The purity of the silicic acid obtained must be tested as directed in *a*, before the operation can be looked upon as successful. These methods, which were formerly often employed to determine the alkalies in silicates, have been in a measure superseded by decomposition with aqueous hydrofluoric acid, and with fluoride of ammonium, both of which can now be readily obtained in a pure form.

δ. Decomposition by fusion with Lime and Lime Salts.

DEVILLE‡ recommends to fuse 1 part of the powdered silicate with from ·3 to ·8 parts of carbonate of lime. I have tried this process, but have not found it answer in the case of many silicates. L. SMITH§ recommends to fuse ·5 to 1 grm. of the powdered silicate with 1 grm. chloride of ammonium, and 8 grm. carbonate of lime. The chloride of ammonium should be in fine grains such as are produced by disturbed crystallization. The carbonate of lime should have been precipitated by carbonate of ammonia in the heat. If the temperature during the fusion rises too high, portions of alkaline chloride may easily be lost. SMITH uses a crucible 95 mm. high, with an upper diameter of 22 mm., and a lower diameter of 16 mm., fixes this in a metal clamp or the iron plate of a special gas furnace,|| so that about 15 mm. remain outside, heats the crucible first above the mixture, then below gently, taking about

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* Zeitschr. f. anal. Chem. 9, 459. † Journ. f. prakt. Chem. 60, 246.

‡ Journ. f. prakt. Chem. 60, 246.

§ *Ib.* 60, 246; Chemical News, 23, 222 and 234.

|| Zeitschr. f. anal. Chem. 11, 87.

5 minutes to decompose all the chloride of ammonium, and then increases the heat, keeping the whole 40 or 60 minutes at a bright red heat. By heating in this way, loss of alkaline chloride is entirely prevented. After the semi-fused mass has cooled treat it according to γ. However, **Smith** says that the whole of the alkalies may be obtained in solution by treating the ignited mass with water, heating for several hours, filtering, and washing the residue. The lime is precipitated by carbonate and a little oxalate of ammonia.

ε. *Decomposition with Hydrochloric or Sulphuric Acid in sealed tubes (under pressure)*, after Al. Mitscherlich.*

Many silicates (and also aluminates) which on digestion with hydrochloric or sulphuric acid in open vessels are either not at all or scarcely attacked, are completely decomposed if heated with hydrochloric acid of 25% HCl, or with a mixture of 3 parts by weight concentrated sulphuric acid and 1 part water in sealed glass tubes for 2 hours at 200° to 210°. For this purpose transfer about 1 grm. of the very fine elutriated or sifted substance to a strong tube of difficultly fusible Bohemian glass fused at one end and somewhat drawn out at the other, add the acid, seal the tube carefully and place it in the wrought iron tube of a metallic bath,† then heat in the manner described. When the tube has cooled, open it cautiously, rinse its contents into a platinum or porcelain dish, and proceed according to II., *a*. The method has this advantage over most others, that any protoxide of iron present is obtained in solution as such and can be accurately determined.

SECOND GROUP.

HYDROCHLORIC ACID—HYDROBROMIC ACID—HYDRIODIC ACID—HYDROCYANIC ACID—HYDROSULPHURIC ACID.

§ 141.

1. HYDROCHLORIC ACID.

1. *Determination.*

Hydrochloric acid may be determined very accurately in the gravimetric as well as in the volumetric way.‡

a. Gravimetric Method.—Determination as Chloride of Silver.

Solution of nitrate of silver, mixed with some nitric acid, is added in excess to the solution of the chloride, the precipitated chloride is made to unite by heating and agitating, washed by decantation and filtration, dried, and ignited. The details of the process have been given in § 115, 1, *a*. Care must be taken not to heat the solution mixed with nitric acid, before the nitrate of silver has been added in excess. As soon as the latter is present in excess, the chloride of silver separates immediately and completely upon shaking or stirring, and the supernatant fluid becomes perfectly clear after standing a short time in a warm place. The determination of hydrochloric acid by means of silver is therefore more readily effected than that of silver by means of hydrochloric acid.

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* Journ. f. prakt. Chem. 81, 108, and 83, 455.

† Such a bath is figured in Journ. f. prakt. Chem. 83, 489; also in Zeitschr. f. anal. Chem. 1, 55.

‡ For the acidimetric estimation of free hydrochloric acid, see § 215.

b. Volumetric Methods.

a. By Solution of Nitrate of Silver.

In § 115, 5, we have seen how the silver in a fluid may be estimated by adding a standard solution of chloride of sodium until no further precipitation ensues; in the same way we may determine also, by means of a standard solution of silver, the amount of hydrochloric acid in a fluid, or of chlorine in combination with a metal. **Pelouze** has used this method for the determination of several equivalent numbers. **Levol*** proposed a modification which serves to indicate more readily the exact point of complete precipitation. To the fluid, which must be *neutral*, he added one-tenth volume of a saturated solution of phosphate of soda. When the whole of the chlorine has been precipitated by the silver, the further addition of the solution of silver produces a yellow precipitate which does not disappear upon shaking the vessel. **Fr. Mohr** has since replaced, with the most complete success, the phosphate of soda by chromate of potassa.

This convenient and accurate method requires a perfectly neutral solution of nitrate of silver of known value. The strength most convenient is, 1 litre = ·1 eq. HCl. I recommend the following method of preparation: Dissolve 18·80 to 18·85 grm. pure fused nitrate of silver in 1100 c.c. water, and filter the solution if required; the solution is purposely made somewhat too strong at first Now weigh off exactly four portions of pure chloride of sodium, each of ·10 to ·18 grm., one after another. The salt should be moderately ignited, not fused, powdered roughly while still warm, and introduced into a small dry tube, that can be well closed. The weighing off is performed by first weighing the filled tube, then shaking out into a dry beaker the quantity required, weighing again, dropping a second portion into beaker No. 2, weighing again, and so on. Each portion is dissolved in 20 to 30 c.c. water, and about 3 drops of a cold saturated solution of pure yellow chromate of potassa added.

Fill a **Mohr**'s burette (in very accurate analysis an **Erdmann**'s float should be used) with the silver solution, and run it slowly, with constant stirring, into the light yellow solution contained in one of the beakers. Each drop produces, where it falls, a red spot, which on stirring disappears, owing to the instant decomposition of the chromate of silver with the chloride of sodium. At last, however, the slight red coloration remains. Now all chlorine has combined with silver, and a little chromate of silver has been permanently formed. Read off the burette and reckon how much silver solution would have been required for ·1 eq. chloride of sodium, *i.e.*, 5·85 grm. Suppose we have used to ·110 chloride of sodium 18·7 c.c. silver solution.

$$\cdot 110 : 5\cdot 85 :: 18\cdot 7 : x \text{ —— } x = 994\cdot 5.$$

Now, without throwing away the contents of the 1st beaker, make a second and third experiment in the same manner, of course always taking notice to regard the same shade of red as the sign of the end. The results of these are reckoned out in the same way as the first. Suppose they gave for 5·85 NaCl 995·0 and 993·0 respectively, we take the mean of the three numbers, which is 994·2, and we now know that we have only to take this number of c.c. of silver solution, and make it up to 1000 c.c. with 5·8 water, in order to obtain a solution of the required strength, *i.e.*, 1000 c.c. = ·1 eq. NaCl. But if 994·2 requires 5·8 water, 1000 requires 5·83. Hence we fill a litre-flask (previously dried or rinsed with a small portion of the solution) up to the "holding" mark with the solution, add 5·83 c.c. water, insert a caoutchouc stopper, and shake.

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* Journ. f. prakt. Chem. 60, 384.

The solution must now be correct; however, to make quite sure, we perform another experiment with it. To this end rinse the empty burette with the new solution, fill it with the same and test with the portion of salt in beaker No. 4. The c.c. used of silver solution must now, if multiplied by ·00585, give exactly the weight of the salt.

Being now in possession of a standard silver solution, and being practised in exactly hitting the transition from yellow to the shade of red, we are in the position to determine with precision hydrochloric acid or chlorine in the form of a metallic chloride soluble in water. The fluid to be tested must be neutral—free acids dissolve the chromate of silver. The solution of the substance is therefore, if necessary, rendered neutral by addition of nitric acid or carbonate of soda (it should be rather alkaline than acid), about 3 drops of the solution of yellow chromate added, and then silver from the burette, till the reddish coloration is just perceptible. The number of c.c. used has only to be multiplied by the equivalent of chlorine or of the metallic chloride and divided by 10000 to give the amount of these respectively present.

If the operator fears he has added too much silver solution, *i.e.*, if the red color is too strongly marked, he may add 1 c.c. of a solution of chloride of sodium containing 5·85 in a litre (and therefore corresponding to the silver solution), and then add the silver drop by drop again. Of course in this case 1 c.c. must be deducted from the amount of silver solution used.

The results are very satisfactory. The fluid to be analysed should be about the same volume as the solutions employed in standardizing the silver solution, and also about the same strength, otherwise the small quantity of silver which produces the coloration will not stand in the same proportion to the chlorine present. This small quantity of silver solution is extremely small, varying between ·05 and ·1 c.c., the inaccuracy hereby arising even in the case of quantities of chlorine differing widely from that originally used in standardizing the silver solution is therefore almost inconsiderable. If the amount of silver solution necessary to impart the coloration always remained the same, we should have simply to deduct the amount in question with all experiments, in order to avoid this small inaccuracy entirely; since however the greater the quantity of chloride of silver the more chromate of silver is required for visible coloration, this method of proceeding would not increase the exactness of the results.

β. By Solution of Nitrate of Silver and Iodide of Starch (PISANI'S method*).

Add to the solution of the chloride, acidified with nitric acid, a slight excess of standard solution of nitrate of silver, warm, and filter.

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* Annal. d. Mines, 10, 83; LIEBIG and KOPP'S Jahresbericht, 1856, 751.

Determine the excess of silver in the filtrate by means of solution of iodide of starch (see p. 240), and deduct this from the amount of silver solution used. The difference shows the quantity of silver which has combined with the chlorine; calculate from this the amount of the latter. Results satisfactory.

γ. *With Solution of Nitrate of Mercury* (LIEBIG's method*); recommended more particularly for the determination of chlorine in the chlorides contained in the urine.

aa. Principle of the method. Nitrate of mercury immediately produces in a solution of urea a heavy white precipitate; solution of chloride of mercury produces no such precipitate. When a solution of nitrate of mercury is mixed with the chloride of an alkali metal, there is formed *chloride of mercury* and nitrate of the alkali. If, therefore, a solution of urea is mixed with chloride of sodium, and a dilute solution of nitrate of mercury is added, drop by drop, the fluid will show in the points of contact a white turbidity, which, however, will immediately disappear upon shaking, as long as the nitrate of mercury continues to decompose the chloride of sodium in the manner just stated; but the moment this double decomposition is complete, an additional drop of the solution of the salt of mercury will produce a permanent white turbidity. Accordingly, if we know the amount and strength of the solution of the salt of mercury required to attain this point, we know also the amount of chlorine in the solution; since 1 eq. mercury in the mercurial solution corresponds to 1 eq. chlorine.

bb. Preparation of the solution of nitrate of mercury. As this solution must be perfectly free from other metals, it is advisable to prepare it with oxide of mercury—precipitated from solution of crystallized chloride of mercury by soda, and thoroughly washed—by dissolving 10·8 grm. of the dry oxide in nitric acid, evaporating the solution to the consistence of syrup, and diluting with water to 550 c.c. Or the solution may be made by dissolving repeatedly recrystallized nitrate of suboxide of mercury in water, with addition of nitric acid, heating to boiling, adding strong nitric acid until no more red fumes escape, evaporating to the consistence of syrup, and diluting with a proper quantity of water to give a solution of tolerably correct strength.

cc. Determination of the strength of the solution. This is effected with the aid of a solution of chloride of sodium of known strength, which LIEBIG prepares by mixing 20 c.c. of a *saturated*† solution of pure rock salt or chemically pure chloride of sodium, with 298·4 c.c. water. A c.c. of this solution contains 20 mgrm. chloride of sodium.

Of this solution of chloride of sodium measure 10 c.c. into a small beaker, and add 3 c.c. of a solution of urea containing 4 grm. in 100 c.c.

Let the solution of mercury to be standardized drop into this mixture from a burette, with shaking, until a perceptible precipitate forms, which on shaking fails to redissolve.*

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* Annal. d. Chem. u. Pharm 85, 297.

† Saturated at the common temperature.

dd. When you have in this way ascertained how many c.c. of the mercurial solution correspond to the 10 c.c. of the solution of common salt = ·2 grm. chloride of sodium, you may use the mercurial solution without further preparation, if you do not mind the trouble of a little calculation. But if you wish to avoid this, you must previously dilute the mercurial solution in a manner that every cubic centimetre may correspond to an integral number of milligrammes of chloride of sodium or chlorine. LIEBIG dilutes it so that 1 c.c. corresponds to ·01 grm. chloride of sodium.

ee. If the test fluid is intended to examine solutions containing a large amount of foreign salts, or an excess of urea, the 10 c.c. of the chloride of sodium solution must be mixed with 5 c.c. of a cold saturated solution of sulphate of soda,† in addition to the 3 c.c. of solution of urea, before the mercurial solution is added. The results are accurate.

δ. Alkalimetrically (after BOHLIG.‡) Add to the solution if necessary carbonate of potash (avoiding a considerable excess) to precipitate alkaline earths or metallic oxides, dilute to 250 c.c., mix, filter and determine the alkalinity in 50 c.c. according to § 220. Then mix 125 c.c. of the filtrate in a ¼ litre flask with pure oxide of silver in excess, fill up with water and shake frequently with exclusion of light. In the course of a few minutes filter through a dry paper, take out 100 c.c. of the filtrate with a pipette (= 50 c.c. of the original fluid) and redetermine the alkalinity. The difference between the alkalinity in the two cases corresponds to the chlorine in the solution. It is well to test a portion of the second filtrate for chlorine. The method is particularly adapted for technical purposes.

Of these volumetric methods of estimating chlorine, the first deserves the preference in all ordinary cases. It cannot be employed, however, for urine, as compounds of oxide of silver with coloring matters, &c., precipitate with the chloride of silver (C. NEUBAUER§). PISANI's method (*b*, *β*) is especially suited for the estimation of very minute quantities of chlorine, but is not applicable when—as in nitre analysis—large quantities of alkaline nitrate are present (p. 236).

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* A mere opalescence of the fluid is disregarded, as this proceeds simply from a trace of foreign metals, that it does not indicate the completion of the reaction is readily seen from the circumstance that it is not increased by a further addition of the mercurial solution.

† The reason of this addition is. that the nitrate of mercury and urea is more readily soluble in pure water than in saline solutions; to attain accurate results, therefore, it is necessary that the solvent power of the fluids should be as nearly as possible the same in the preliminary determination of the strength of the mercurial solution as in the subsequent analytical process.

‡ Zeitschr. f. anal. Chem. 9, 314.

§ In order to apply the method also to urine, PRIBRAM (Zeitschr. f. anal. Chem. 9, 428) heats 10 c.c. urine with 50 c.c. of solution of pure permanganate of potassa (containing 1 or 2 grm. in 1 litre) to gentle ebullition, filters off the brown flocks, washes and determines the chlorine in the filtrate by *b*, *a*.

II. *Separation of Chlorine from the Metals.*

a. In Soluble Chlorides.

The same method as in I., *a*. The metals in the filtrate are separated from the excess of the salt of silver by the methods which will be found in Section V. Chlorides soluble in water may also be completely decomposed by cold digestion with oxide or carbonate of silver. Chloride of silver is obtained, while the metal combined with the chlorine is converted into oxide or carbonate and either remains in solution or falls down with the chloride of silver. Take care that no traces of oxide or carbonate of silver pass into the filtrate.

Bichloride of tin, *chloride of mercury*, the *chlorides of antimony*, the *green chloride of chromium* and *bichloride of platinum*, form exceptions from the rule.

α. From *bichloride of tin*, nitrate of silver would precipitate, besides chloride of silver, a compound of binoxide of tin and oxide of silver. To precipitate the tin, therefore, the solution is mixed with concentrated solution of nitrate of ammonia, boiled, allowed to deposit, decanted, and filtered (compare § 126, 1 *b*), and the chlorine in the filtrate is precipitated with solution of silver. LÖWENTHAL, the inventor of this method, has proved its accuracy.*

β. When *chloride of mercury* is precipitated with solution of nitrate of silver, the chloride of silver thrown down contains an admixture of mercury. The mercury is, therefore, first precipitated by sulphuretted hydrogen, and the chlorine in the filtrate determined as directed in § 169.

γ. *The chlorides of antimony* are also decomposed in the manner described in β. The separation of basic salt upon the addition of water may be avoided by addition of tartaric acid. The sulphide of antimony should be tested for chlorine.

δ. Solution of silver fails to precipitate the whole of the chlorine from solution of the *green chloride of chromium* (PÉLIGOT). The chromium is, therefore, first precipitated with ammonia, the fluid filtered, and the chlorine in the filtrate precipitated as in I., *a*.

ε. From *bichloride of platinum* nitrate of silver throws down a compound of protochloride of platinum and chloride of silver (COMAILLE†). We may either ignite the bichloride of platinum in a current of hydrogen and pass the hydrochloric acid produced into solution of silver (BONSDORFF); or we may evaporate the solution with carbonate of soda, fuse the residue in a platinum crucible and determine the chloride in the aqueous solution of the fusion. Or, thirdly, we may (after TOPSÖE‡) digest the moderately dilute solution in the cold with zinc clippings till hydrogen ceases to escape, add ammonia in excess, heat on a water-bath till the fluid is fully decolorized, all the platinum being precipitated, and finally determine the chlorine in the filtrate.

b. In Insoluble Chlorides.

α. Chlorides soluble in Nitric Acid.

Dissolve the chloride in nitric acid, without applying heat, and proceed as in I., *a*.

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* Journ. f. prakt. Chem. 66, 371.

† Zeitschr. f. anal. Chem. 6, 121.

‡ *Ib.* 9, 30.

β. Chlorides insoluble in Nitric Acid (chloride of lead, chloride of silver, subchloride of mercury).

aa. Chloride of lead is decomposed by digestion with alkaline bicarbonate and water. The process is exactly the same as for the decomposition of sulphate of lead (§ 132, II., *b*, *β*).

bb. Chloride of silver is ignited in a porcelain crucible, with 3 parts of carbonate of soda and potassa, until the mass commences to agglutinate. Upon treating with water, the metallic silver is left undissolved; the solution contains the alkaline chloride, which is then treated as in I., *a*.

Chloride of silver may also be readily decomposed by long digestion with pure iron (reduced by hydrogen) and dilute sulphuric acid. Zinc may be used instead of iron but it does not answer so well. The separated metallic silver may be washed, heated with dilute sulphuric acid, washed again and weighed; it must afterwards be ascertained, however, whether it dissolves in nitric acid. The chlorine is determined in the chloride of iron or zinc as in I., *a*.

cc. Subchloride of mercury is decomposed by digestion with solution of soda or potassa. The hydrochloric acid in the filtrate is determined as in I., *a*. The suboxide of mercury is dissolved in nitric or nitrohydrochloric acid, and the mercury determined as directed in § 117 or § 118.

c. The soluble chlorides of the metals of the fourth, fifth, and sixth groups may generally be decomposed also by sulphuretted hydrogen, or, sulphide of ammonium. The hydrochloric acid in the filtrate is determined as in § 169. It must not be omitted to test the precipitated sulphides for chlorine. Several chlorides, chloride of cadmium for instance, give sulphides free from chlorine with sulphide of ammonium but not with sulphuretted hydrogen.

d. In many metallic chlorides, for instance, in those of the first and second groups, the chlorine may be determined also by evaporating with sulphuric acid, converting the base thus into a sulphate, which is then ignited and weighed as such; the chlorine being calculated from the loss. This method is not applicable in the case of chloride of silver and chloride of lead, which are only imperfectly and with difficulty decomposed by sulphuric acid; nor in the case of chloride of mercury and bichloride of tin, which sulphuric acid fails almost or altogether to decompose.

Supplement.

Determination of Chlorine in the Free State.

§ 142.

Chlorine in the free state may be determined both in the volumetric and in the gravimetric way. The volumetric methods, however, deserve the preference in most cases. They are very numerous.

I shall only here adduce that one which is undoubtedly the most accurate and at the same time the most convenient.*

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* Compare "Chlorimetry" in the Special Part.

1. *Volumetric Method.*

With Iodide of Potassium (*after* BUNSEN).

Bring the chlorine, in the gaseous form or in aqueous solution, into contact with an excess of solution of iodide of potassium in water. Each eq. chlorine liberates 1 eq. iodine, which remains dissolved in the excess of iodide of potassium. By determining the liberated iodine by means of hyposulphite of soda as in § 146, you will accordingly learn the quantity of chlorine, and, in fact, with the greatest accuracy. If you have to determine the chlorine of chlorine water, measure a portion off with a pipette. So as to prevent any of the gas entering the mouth, connect the upper end of the pipette with a tube containing moist hydrate of potassa laid between wool. When the pipette has been correctly filled allow its contents to flow, with stirring, into an excess of solution of iodide of potassium (1 in 10). There is no difficulty about knowing whether the latter is sufficiently in excess, for if not, a black precipitate is formed. If the chlorine is evolved in the gaseous condition, you may employ either the apparatus given in § 130, I., *e*, *β*, or the following, which is especially suitable where the chlorine is not pure, but is mixed with other gases.

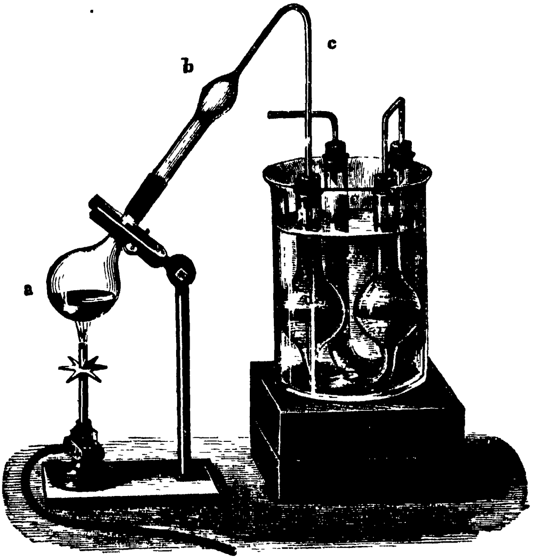

Fig. 95.

a is a little flask, from which the chlorine is evolved by boiling the substance with hydrochloric acid, a small lump of magnesite being added; it is connected with the tube, *b*, by means of a flexible tube. The latter must be free from sulphur—should it contain sulphur it is well boiled with dilute potassa and then thoroughly washed. The thinner tube, *c*, which has been fused to the bulb of *b*, leads through the caoutchouc stopper (which has been deprived of sulphur) to the bulbed U-tube, *d*, which contains solution of iodide of potassium, and which for safety is connected with the plain U-tube, *e*, also containing iodide of potassium solution. Both tubes stand in a beaker filled with water. The apparatus offers the advantages that the fluid cannot return, that the iodide of potassium remains cold, and that the absorption is complete. After all the chlorine has been expelled by boiling long enough, rinse *d* and *e* out into a beaker and titrate with standard hyposulphite of soda (§ 146).

2. *Gravimetric Method.*

The fluid under examination, which must be free from sulphuric acid, say, for instance, 30 grm. chlorine water, is mixed in a stoppered bottle, with a slight excess of hyposulphite of soda, say ·5 grm., the stopper inserted, and the bottle kept for a short time in a warm place; after which the odor of chlorine is found to have gone off. The mixture is then heated to boiling with some hydrochloric acid in excess, to destroy the excess of hyposulphite of soda, filtered, and the sulphuric acid in the filtrate determined by baryta (§ 132). 1 eq. sulphuric acid corresponds to 2 eq. chlorine (Wicke[*]).

In fluids containing, besides free chlorine, also hydrochloric acid, or a metallic chloride, the chlorine existing in a state of combination may be determined, in presence of the free chlorine, in the following way:—

A weighed portion of the fluid is mixed with solution of sulphurous acid in excess, after some time nitric acid is added, and then chromate of potassa to destroy the excess of sulphurous acid, and the whole of the chlorine is precipitated as chloride of silver. The quantity of the free chlorine is then determined in another weighed portion, by means of iodide of potassium; the difference gives the amount of combined chlorine.[†]

Having thus seen in how simple and accurate a manner the quantity of free chlorine may be determined by Bunsen's method, it will be readily understood that all oxides and peroxides which yield chlorine when heated with hydrochloric acid, may be analysed by heating them with concentrated hydrochloric acid, with addition of a small lump of magnesite, and determining the amount of chlorine evolved.

§ 143.

2. Hydrobromic Acid.

I. *Determination.*

a. Gravimetric Methods.

Estimation as bromide of silver. Free hydrobromic acid—in a solution free from hydrochloric acid or chlorides—is precipitated by silver solution, and the further process is conducted as in the case of hydrochloric acid (§ 141). For the properties of bromide of silver, see § 94, 2. The results are perfectly accurate.

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[*] Annal. d. Chem. u. Pharm. 99, 99.

[†] If chlorine water is mixed at once with nitrate of silver, $\frac{5}{6}$ only of the chlorine is obtained as chloride of silver: $6Cl + 6AgO = 5AgCl + AgO,ClO_5$ (H. Rose, Weltzien, Annal. d. Chem. u. Pharm. 91, 45). If chlorine water is mixed with ammonia in excess, there are formed at first chloride of ammonium and hypochlorite of ammonia, the latter then gradually decomposes into nitrogen and chloride of ammonium; however, a little chlorate of ammonia is also formed besides (Schönbein, Journ. f. prakt. Chem. 84, 386; Zeitschrift f. analyt. Chem. 2, 59).

b. Volumetric Methods.

Like hydrochloric acid and the chlorine in alkaline metallic chlorides, bromine may be estimated in the analogous compounds by *standard silver solution* (§ 141, I., *b*, *α*), by *solution of silver and iodide of starch* (§ 141, I., *b*, *β*), and by the *alkalimetric method* (§ 141, I., *b*, *δ*). But these methods are seldom applicable, as they cannot be used in the presence of hydrochloric acid and metallic chlorides.

The following methods must therefore be detailed; they are especially useful for the estimation of small quantities of bromine in solutions containing chlorides, but in point of accuracy they leave much to be desired.[*]

α. With chlorine water and chloroform (*after* A. REIMANN[†]). This method depends on the facts that chlorine when added to bromides first liberates the bromine and then combines with it, and that bromine colors chloroform yellow or orange, while chloride of bromine merely communicates a yellowish tinge to that fluid. The process is as follows:—Mix the liquid containing a bromide of an alkali metal in neutral solution, in a stoppered bottle with a drop of pure chloroform about the size of a hazel-nut, then add standard chlorine water from a burette, protected from the light by being surrounded with black paper. On shaking, the chloroform becomes yellow, on further addition of chlorine water, orange, then yellow again, and lastly—at the moment, when 2 eq. chlorine have been used for 1 eq. bromine—yellowish white ($KBr + 2Cl = KCl + BrCl$). Considerable practice and skill are required before the operator can tell the end-reaction. He will be assisted by placing the bottle on white paper and comparing the color of the chloroform with that of a dilute solution of yellow chromate of potassa of the required color. The strength of the chlorine water should depend on the amount of the bromine to be determined. It should be so adjusted that about 100 c.c. may be used. The chlorine water is standardized with iodide of potassium and hyposulphite of soda (§ 142, 1). The method is especially suited for the determination of small quantities of bromine in mother liquors, kelp, &c. The results are approximate: *e.g.*, ·0180 instead of ·0185—·055 instead of ·059—·0112 instead of ·0100, &c. If the fluid contains organic substances, it is—after being rendered alkaline with caustic soda—evaporated to dryness, the residue ignited in a silver dish, extracted with water, the solution neutralized exactly with hydrochloric acid, and then tested.

β. With chlorine water and the application of heat (*after* FIGUIER[‡]). This method is based upon the circumstances that 1 eq. chlorine liberates from a solution of a metallic bromide 1 eq. bromine, and that bromine imparts a yellow color to an aqueous solution, and escapes readily upon boiling, the yellow tint of the solution disappearing with the escape of the bromine. The chlorine is used in dilute aqueous solution. It is standardized immediately before use, by making it act upon a solution of bromide of sodium of known strength, acidified with a few drops of hydrochloric acid (or more simply with iodide of potassium and hyposulphite of soda, according to § 142, 1). The mother liquor is heated in a flask nearly to ebullition; chlorine water is then added from a burette covered with black paper, and the mixture heated for about 3 minutes, whereupon the yellow tint imparted to the fluid by the addition of the chlorine water will disappear again; the mixture is now allowed to cool for 2 minutes, after which some more chlorine water is dropped into it, heat again applied, and the same process repeated until further addition of chlorine water fails to impart a yellow color to the fluid. Should the experiment last several hours, the strength of the chlorine water must be determined once more at the end of the process, and the calculation of the results based upon the mean of the two experiments. Alkaline fluids must be slightly acidified with hydrochloric acid. Protoxide of iron, protoxide of manganese, iodine, and organic matters must not be present. Mother liquors colored yellow by organic matter should be evaporated to dryness, the residue gently ignited, then treated with water, and the fluid filtered. In evaporating the solutions to dryness, carbonate of soda must be added, since chloride and bromide of magnesium evolve hydrochloric and hydrobromic acids in the process.

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[*] Compare § 169.

[†] Annal. d. Chem. u. Pharm. 115, 140.

[‡] Annal. de Chim. et de Phys. 33, 303; and Journ. f. prakt. Chem. 54, 293. Proposed to effect the determination of bromine in mother liquors.

From my own experiments it appears that the process is hastened, and the results improved by providing the flask used for boiling the liquor with a cork containing three perforations. Through one carbonic acid is passed to the bottom of the fluid, through another the point of the burette—in this case somewhat lengthened—passes, and through the third the carbonic acid and the bromine escape. The fluid is kept in gentle ebullition throughout the operation.

γ. HEINE's *colorimetric method.*[*] The bromine is liberated by means of chlorine, and taken up with ether; the solution is compared, with respect to color, with an ethereal solution of bromine of known strength, and the quantity of bromine in it thus ascertained. FEHLING[†] obtained satisfactory results by this method. It will at once be seen that the amount of bromine contained in the fluid to be analysed must be known in some measure, before this method can be resorted to. As the brine examined by FEHLING could contain at the most ·02 grm. bromine in 60 grm., he prepared ten different test fluids, by adding to ten several portions of 60 grm. each of a saturated solution of common salt increasing quantities of bromide of potassium, containing respectively from ·002 grm. to ·020 grm. bromine. He added an equal volume of ether to the test fluids, and then chlorine water, until there was no further change observed in the color of the ether. It being of the highest importance to hit this point exactly, since too little as well as too much chlorine makes the color appear lighter, FEHLING prepared three samples of each test fluid, and then chose the darkest of them for the comparison. 60 grm. are now taken[‡] of the mother liquor to be examined, the same volume of ether added as was added to the test fluids, and then chlorine water. Every experiment is repeated several times. Direct sunlight must be avoided, and the operation conducted with proper expedition. In my opinion it is well to replace the ether by chloroform or bisulphide of carbon. CAIGNET[§] substituted hypochlorite of soda for the chlorine water, and removed the colored bisulphide of carbon from time to time.

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[*] Journ. f. prakt. Chem. 36, 184. Proposed to effect the determination of bromine in mother liquors.

[†] Journ. f. prakt. Chem. 45, 269.

[‡] The best way is to take them by measure.

[§] Zeitschr. f. anal. Chem. 9, 427.

II. *Separation of Bromine from the Metals.*

The metallic bromides are analysed exactly like the corresponding chlorides (§ 141, II., *a* to *d*), the whole of these methods being applicable to bromides as well as chlorides. In the decomposition of bromides by sulphuric acid (§ 141, II., *d*), porcelain crucibles must be used instead of platinum ones, as the latter would be attacked by the liberated bromine. Some bromides it must be remembered are not completely decomposed by sulphuric acid; for instance, bromide of mercury is not. The soluble bromides may be converted into chlorides by evaporation with hydrochloric acid and excess of chlorine water; but this process cannot be applied where the chloride is liable to be carried away with the steam; for instance, in the case of bromide of mercury.

Supplement.

Determination of Free Bromine.

§ 144.

Free bromine in aqueous solution, or evolved in the gaseous form, is caused to act on excess of solution of iodide of potassium. Each eq. bromine liberates 1 eq. iodine, which is most conveniently determined by means of hyposulphite of soda (§ 146). As regards the best mode of bringing about the action of the bromine on the iodide of potassium, compare § 142, 1.

The determination of free bromine in presence of hydrobromic acid or metallic bromides is effected in the same manner as that of free chlorine in presence of hydrochloric acid (see § 142).

§ 145.

3. Hydriodic Acid.

I. *Determination.*[*]

a. Gravimetric Methods.

α. Estimation as iodide of silver. If you have hydriodic acid in solution, free from hydrochloric and hydrobromic acids, precipitate with nitrate of silver, and proceed exactly as with hydrochloric acid (§ 141). If the solution were colored with free iodine, first add sulphurous acid cautiously till the color is removed. The particles of iodide of silver adhering to the filter are not reduced on incineration, but a little of the iodide is liable to volatilize if the heat is too high. Hence the filter should be got as clean as possible, and the heat during incineration should not be unduly raised. For the properties of iodide of silver, see § 94, 3. The results are perfectly accurate.

β. Estimation as protiodide of palladium. The following method, recommended first by Lassaigne, is resorted to exclusively to effect the separation of hydriodic acid from hydrochloric and hydrobromic acids, for which purpose it is extremely well adapted. The solution may not contain any alcohol. Acidify it slightly with hydrochloric acid, and add a solution of protochloride of palladium, as long as a precipitate forms; let the mixture stand from 24 to 48 hours in a warm place, filter the brownish-black precipitate off on a weighed filter, wash with warm water, and dry at 100°, until the weight remains constant. For the properties of the precipitate, see § 94, 3. This method gives very accurate results. Instead of simply drying the protiodide of palladium, and weighing it in that form, you may ignite it in a current of hydrogen in a crucible of porcelain or platinum,* and calculate the iodine from the residuary palladium (H. ROSE.) Compare § 122, 1.

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[*] For the methods to be adopted in the presence of bromine and chlorine, see

b. Volumetric Methods.

a. The methods given for hydrochloric acid by *precipitating with silver solution* (§ 141, I., *b*, *a*), by *silver solution and iodide of starch* (§ 141, I., *b*, *β*), and also by *alkalimetry* (§ 141, I., *b*, *δ*) may be used for hydriodic acid and alkaline iodides; the absence of chlorine and bromine being of course presupposed.

β. With nitrous acid and bisulphide of carbon. This excellent method has been in frequent use in my laboratory for a length of time, it may be used for small or large quantities of iodine. We require :—

aa. Solution of iodide of potassium of known strength. Made by drying the pure salt at 180° (see p. 105) and dissolving an exactly weighed quantity (about 5 grm.) to 1 litre.

bb. Solution of hyposulphite of soda containing about 13 or 13·5 grm. of the pure crystallized salt in 1 litre.

cc. Solution of nitrous acid in sulphuric acid. Prepared by passing nitrous acid gas into sulphuric acid to saturation.

dd. Pure bisulphide of carbon (p. 91).

ee. Solution of bicarbonate of soda. Made by dissolving 5 grm. in 1000 c.c. cold water and adding 1 c.c. of hydrochloric acid to the solution.

Begin by standardizing the hyposulphite as follows. Take a well-stoppered bottle of about 400 c.c. capacity, transfer to it 50 c.c. of the iodide of potassium solution, add about 150 c.c. water, 20 c.c. bisulphide of carbon, some dilute sulphuric acid, and 10 drops of the solution of nitrous acid in sulphuric acid. Insert the stopper and shake the bottle violently for some time, allow to settle, and ascertain by adding a few more drops of the nitrous acid that the whole of the iodine has been liberated. Shake again, allow to settle, and pour the supernatant fluid as completely as possible into a flask, leaving the bisulphide of carbon in the bottle, add 200 c.c. water to the latter, shake well, pour off the water into the flask and repeat the washing till the last water has no acid reaction. To the contents of the flask add 10 c.c. bisulphide of carbon, shake well, pour off into a second flask, wash the bisulphide a little, and finally shake the contents of the second flask again with some fresh bisulphide, which should now be barely tinged. Collect the bisulphide from both flasks on a filter moistened with water, wash it till the washings are no longer acid, place the funnel in the bottle and pierce the point of the filter so that the bisulphide from all the operations may be mixed. Add 30 c.c. of the bicarbonate of soda and then the hyposulphite from a burette, with continual shaking, till the bisulphide has lost its color. The number of c.c. of hyposulphite used will correspond to the iodine in 50 c.c. of iodide of potassium solution.

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* This substance is not injured by the operation.

The analysis is performed exactly as above. The hyposulphite requires to be standardized before every fresh series of experiments, as it is liable to slight alteration. The presence of chlorides has no influence whatever on the results. In determining minute quantities of iodine let the solutions be ten times weaker, and use smaller quantities and smaller vessels.

The results are entirely concordant and exact.

γ. *With permanganate of potash, after* **Reinige.*** This method takes but little time and yields good results. It depends on the fact that alkaline iodides decompose with permanganate of potash in accordance with the following equation—

$$KI + 2(KO,Mn_2O_7) = KO,IO_5 + 2KO + 4MnO_2.$$

This reaction was first suggested by **Péan de Saint-Gilles**† as the basis of a volumetric method for estimating iodine. A boiling heat favors the decomposition. In the case of very dilute solutions some alkaline carbonate is added to commence the change. The presence of chlorides and bromides is without effect.

We require solutions of permanganate of potash and hyposulphite of soda each containing about 5 grm. per litre. The permanganate is standardized either according to § 112, 2, *a*, or by a solution of iodide of potassium of known strength, in the manner described below. The hyposulphite is used to estimate the excess of permanganate, we must therefore standardize it on the latter. The reaction is as follows: $KO,Mn_2O_7 + 6(NaO,S_2O_2) = 2MnO_2 + 3(NaO,S_4O_5) + KO + 3NaO$. Measure off about 1 c.c. of the permanganate, add a quantity of water, a few drops of carbonate of soda, and then hyposulphite from a burette till the red color is gone; the point is not difficult to hit in very dilute solutions notwithstanding the presence of the brown hydrated peroxide of manganese.

The solution to be analysed should contain all the iodine in the form of alkaline iodide. Add a little carbonate of potash or soda, heat to gentle boiling, and add the permanganate till the fluid containing the brown precipitate in suspension assumes a distinctly red color, which does not disappear on repeating boiling. To detect the color better remove the flame a few seconds from the flask to enable the precipitate to subside. Now transfer the whole to a 500 c.c. measuring flask, allow to cool, fill up to the mark, remove 100 c.c. with a pipette, and titrate with hyposulphite till the fluid is decolorized. Multiply the amount of the latter used by 5, calculate it into permanganate, and deduct this from the amount of permanganate used; the remainder corresponds to the amount of iodine present. It is not so well, as **Reinige** directs, to titrate the excess of permanganate directly in the fluid with the brown precipitate suspended in it.

It need hardly be mentioned that organic and other reducing matter must be carefully excluded.

δ. *With silver solution and iodide of starch* (**Pisani**‡). We require standard decimal silver solution (p. 355) and standard iodide of starch (p. 240).

The solution to be analysed should contain the iodine in the form of alkaline iodide. It may be neutral or slightly acid. Add a little pure precipitated carbonate of lime, then a half or one c.c. of iodide of starch and then silver solution from the burette with stirring, till the iodide of starch has lost its color. Determine the small quantity of silver solution necessary to decolorize the iodide of starch employed, and after deducting this from the quantity of silver solution used in the above experiment, you will find the quantity corresponding to the iodine present. The method, it will be seen, depends on the silver solution first decomposing the metallic iodide, then the iodide of starch, and finally any chloride present. The method is soon executed, and in the absence of chlorides and bromides yields good results. In the presence of small quantities of chlorides the results are still approximate, but much chloride entirely destroys their accuracy, as the precipitated chloride of silver is not decomposed with sufficient rapidity by the metallic iodide and iodide of starch present. Bromides interfere still more than chlorides.

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* Zeitschr. f. anal. Chem. 9, 39.

† Compt. rend. 46, 624.

‡ *Ib.* 44, 352.

ε. *By distillation with sesquichloride of iron* (DUFLOS). When hydriodic acid or a metallic iodide is heated in a retort with solution of pure sesquichloride of iron, the whole of the iodine escapes with the aqueous vapor, and protochloride of iron is formed ($Fe_2Cl_3 + HI = 2FeCl + HCl + I$). The iodine passing over is received in solution of iodide of potassium and determined by hyposulphite of soda, as directed § 146. In employing this method it must be borne in mind that the sesquichloride of iron must be free from chlorine and nitric acid. It is best to prepare it from sesquioxide of iron and hydrochloric acid. We must not forget too that the separated iodine is liable to act on cork and caoutchouc; the apparatus should therefore be constructed according to fig. 78, p. 179.

ζ. KERSTING's method* consists in *precipitating with standard protochloride of palladium* till no further turbidity is produced. It gives good results, but is somewhat tedious and therefore not much used. A. and F. DUPRÉ's method† depends on the *action of chlorine water upon alkaline iodide*. This gives good results only in the absence of chlorides.‡

η. H. STRUVE's *colorimetric method*§ may be used in many cases. In this method the amount of iodine is estimated by the depth of color which the separated iodine gives to a measured quantity of bisulphide of carbon.

II. *Separation of Iodine from the Metals.*

The metallic iodides are in general analysed like the corresponding chlorides. From iodides of the alkali metals containing free alkali the iodine may be precipitated as iodide of silver, by first saturating the free alkali almost completely with nitric acid, then adding solution of nitrate of silver in excess, and finally nitric acid to strongly acid reaction. If an excess of acid were added at the beginning, free iodine might separate, which is not converted completely into iodide of silver by solution of nitrate of silver. In compounds soluble in water the iodine may generally be precipitated as protiodide of palladium; you may also determine the base in one portion (decomposing the compound with concentrated sulphuric acid), and the iodine in another portion according to I., *b*, ε.

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* Annal. d. Chem. u. Pharm. 87, 25. † *Ib.* 94, 365.

‡ H. ROSE's Handb. d. anal. Chem. 6 Aufl. von FINKENER, ii. 628; and also my own experiments.

§ Zeitschr. f. anal. Chem. 8, 230.

Iodine cannot be separated from platinum directly with nitrate of silver, as insoluble platinum salts would be thrown down with the iodide of silver. For this purpose H. TOPSÖE* recommends the following process:—Dissolve the substance in a good amount of water, add solution of bisulphite of soda and sulphurous acid, heat on a water-bath till the color has entirely disappeared, and the platinum is consequently converted into protosulphite. In this operation a white flocculent precipitate of sulphite of protoxide of platinum and soda which is difficultly soluble, separates; it redissolves on addition of sulphurous acid. After heating on the water-bath for some time, allow to cool completely, precipitate with silver solution, which should not be added in large excess, add nitric acid, heat for about an hour to redissolve the sulphite of silver first thrown down with the iodide, and then filter off the latter. Occasionally it is to be preferred to add sulphurous acid instead of the sulphite of soda, and then, when the fluid has been heated and the color has gone, to add an excess of ammonia. In this way the platinum compound is not thrown down, and the sulphite of silver does not separate after the addition of silver solution till nitric acid is added, and is immediately redissolved by the excess of the same.

For the analysis of insoluble iodides, especially the iodides of silver and lead, the protoiodide of mercury and the subiodide of copper, E. MEUSEL† strongly recommends hyposulphite of soda, in which these salts dissolve. Very little water should be used, and as small a quantity of the hyposulphite as possible. The metal is precipitated from the solution by sulphide of ammonium in the form of sulphide. Evaporate the filtrate with soda and heat the residue in a platinum dish to incipient redness to destroy the hyposulphite and tetrathionate of soda. Dissolve the fusion in water by the aid of heat, and determine the iodine in it by I., *b*, *ε*. A large quantity of sesquichloride of iron will be required to decompose the sulphite of soda; the residue in the retort should have a deep reddish-brown color.

Iodide of silver may be decomposed also by fusing with carbonate of soda (see p. 360), but not by igniting in a current of hydrogen, and not completely by zinc or iron. Protoiodide of mercury may be easily decomposed by distilling with 8 or 10 parts of a mixture of 1 part cyanide of potassium and 2 parts quick lime. For the apparatus, see fig. 84, p. 250; *ab* is filled with magnesite (H. ROSE‡). Protoiodide of palladium may be decomposed by igniting in hydrogen. Subiodide of copper, and many other iodides may be decomposed by boiling with potash or carbonate of soda. Portions of metal, which may pass into the alkaline solution, may be thrown down by sulphide of ammonium, or by acidifying with acetic acid, and passing sulphuretted hydrogen.

SUPPLEMENT.

DETERMINATION OF FREE IODINE.

§ 146.

The determination of free iodine is an operation of great importance in analytical chemistry, since, as BUNSEN§ first pointed out, it is a means for the estimation of all those substances which, when brought in contact with iodide of potassium, separate from the same a definite quantity of iodine (*e.g.*, chlorine, bromine, &c.), or, when boiled with hydrochloric acid, yield a definite quantity of chlorine (*e.g.*, chromic acid, peroxide of manganese, &c.). By causing the chlorine produced to act on iodide of potassium, we obtain the equivalent quantity of free iodine.

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* Zeitschr. f. anal. Chem. 9, 30.

† *Ib.* 9, 208.

‡ *Ib.* 2, 1.

§ Annal. d. Chem. u. Pharm. 86, 265.

Of the various methods which have been proposed for the estimation of free iodine, the oldest is that of Schwarz.[*] It is based upon the following reaction: $2\,(NaO,S_2O_2) + I = NaI + NaO,S_4O_5$. 24·8 grm. pure crystallized hyposulphite of soda are dissolved to 1 litre. 1000 c.c. of the solution correspond to 12·685, *i.e.*, to ·1 eq. iodine. This solution is added to the solution of the substance in iodide of potassium, until the fluid appears bright yellow, 3 or 4 c.c. thin and very clear starch paste are then added, which must produce blue coloration, and finally again hyposulphite of soda, until the blue fluid is decolorized.

This method, though in itself excellent, is open to this objection—that it is difficult to obtain a solution of absolutely exact value by weighing off hyposulphite of soda, as the salt is not readily procurable in a perfectly pure and dry condition, and although the solution does not change rapidly or to any great extent, it is still liable to gradual alteration, especially under the influence of light.

Bunsen's researches on the volumetric estimation of iodine cited above, produced a very important and beneficial effect on the whole domain of chemical analysis. His process depends on the fact, that when iodine comes in contact with an aqueous solution of sulphurous acid, a decomposition takes place in accordance with the equation, $I + 2HO + SO_2 = HI + HO,SO_3$, provided the solution does not contain more than ·04 to ·05 per cent of anhydrous sulphurous acid. If the solution is more concentrated, another reaction also takes place to a greater or less extent—namely, $HI + HO,SO_3 = I + 2HO + SO_2$.

In this method, a solution of iodine in iodide of potassium containing a known quantity of free iodine is employed, and we commence by determining the relation between it and a sufficiently dilute solution of sulphurous acid. In applying the method, the iodine to be estimated is dissolved in iodide of potassium, the standard sulphurous acid is added to decoloration, then thin starch-paste, and finally standard iodine solution till the blue color of iodide of starch is just visible.

We calculate now the c.c. of iodine solution which correspond to the sulphurous acid employed, and deduct therefrom the c.c. of iodine added to destroy the excess of sulphurous acid. The remainder gives the number of c.c. of iodine solution which contain a quantity of iodine equal to that in the substance analysed.

On account of the rapidity with which solution of sulphurous acid changes, this method is somewhat inconvenient, and has given place to the following, which is now universally employed. It retains the basis of Bunsen's method, but substitutes hyposulphite of soda for sulphurous acid, employing the reaction of Schwarz's method. With F. Mohr[†] I give this "combined method" the preference, because, first, we are not bound to a definite strength of the hyposulphite; secondly, the solution of hyposulphite is far less affected by the oxygen of the air than sulphurous acid; and thirdly, it loses nothing by evaporation. Finkener* even says, that the use of hyposulphite makes the method more accurate, his experiments having shown that in using Bunsen's method the results differ; if, on one occasion, we add the sulphurous acid to the iodine, and, on another, the iodine to the sulphurous acid.

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[*] Anleit. zu Maassanal. Nachträge, 1853, 22.

[†] Lehrb. d. chem.-analyt. Titrirmethode, 3 Aufl. 256.

a. Requisites for the Combined Method.

α. *Iodine solution of known strength.* Dissolve 6·2 to 6·3 grm. iodine with the aid of about 9 grm. iodide of potassium (free from iodic acid) to about 1200 c.c.

β. *Solution of hyposulphite of soda.* Dissolve 12·2 to 12·3 grm. of the pure and dry salt to about 1200 c.c.

γ. *Solution of iodide of potassium.* Dissolve 1 part of the salt (free from iodic acid) in about 10 parts of water. The solution must be colorless and must remain so immediately after the addition of dilute sulphuric or hydrochloric acid (either must be iron-free).

δ. *Starch solution.* Stir the purest starch powder gradually with about 100 parts cold water and heat to boiling with constant stirring. Allow to cool quietly, and pour off the fluid from any deposit. The solution should be almost clear and free from all lumps. The starch solution is best prepared fresh before each series of experiments.

b. Preliminary Determinations.

α. *Determination of the relation between the Iodine Solution and Hyposulphite Solution.*

Fill two burettes with the solutions. Run 20 c.c. of the hyposulphite into a beaker, add some water and 3 or 4 c.c. starch solution, then add the iodine till a blue coloration is just produced. If you have added a drop too much, run in one or two drops more of the hyposulphite, and then more cautiously the iodine solution. After a few minutes read off the height of the fluid in both burettes. Suppose we had used 20 c.c. hyposulphite to 20·2 c.c. iodine.

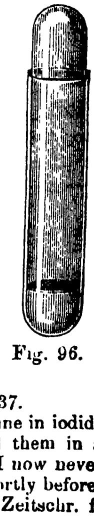

Fig. 96.

β. *Exact Determination of the Iodine in the Solution.*

This is done immediately before each series of analyses with the aid of an exactly weighed quantity of pure and dry iodine. Experience has convinced me that solution of iodine in iodide of potassium, even when kept cool and in the dark, is much more liable to change than is usually supposed.†

The tubes, fig. 96, are heated and allowed to cool in the desiccator. Now transfer to the inner tube about ·2 grm. pure resublimed iodine‡ (p. 104), lay the tube obliquely in a sand bath, heat till the iodine melts, then remove the tube and allow it to cool a little in a very oblique position so that you can hold it with your hand, place the larger tube over it, allow to cool entirely in the desiccator, weigh and find in this manner the exact amount of iodine in the tube. Now place the inner tube in a stoppered bottle, containing 10 c.c. of solution of iodide of potassium. Of course, the outer tube must be put in the bottle too if any trace of iodine adheres to it. As soon as the iodine is all dissolved, add water and then hyposulphite from a burette till the color is gone; now add 3 or 4 c.c. of starch-paste and iodine solution (*a*, *a*) from a second burette till a blue tinge just appears. Having read off both burettes, the following simple calculation will give you the iodine in the solution *a*, *a*:—

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* H. Rose, Handb. d. anal. Chem. 6 Aufl. von Finkener, 2, 937.

† I filled several small well-stoppered bottles with some solution of iodine in iodide of potassium, whose standard had been accurately determined, and placed them in a cellar. Even in the course of a few weeks the standard had altered. I now never rely on the strength of a solution of iodine, unless I have determined it shortly before.

‡ In respect of the preparation of absolutely pure iodine see Stas, Zeitschr. f. anal. Chem. 6, 419.

Suppose we had weighed off ·150 grm. iodine, and used 29·5 c.c. hyposulphite and ·3 c.c. iodine solution.

From *b*, *a*, we know that 20 c.c. hyposulphite correspond to 20·2 c.c. iodine solution; 29·5 c.c. therefore correspond to 29·8 c.c.

Now 29·5 c.c. hyposulphite correspond to ·150 grm. iodine + ·3 c.c. iodine solution.

But 29·5 c.c. hyposulphite also correspond to 29·8 c.c. iodine solution.

∴ ·150 grm. iodine + ·3 c.c. iodine solution = 29·8 c.c. iodine solution.

∴ ·150 grm. iodine = 29·5 c.c. iodine solution.

∴ ·1 c.c. iodine solution = ·0050847 grm. iodine.

The experiment just described is repeated and the mean of the two results taken, provided they exhibit sufficient uniformity.

γ. Dilution of the standard fluids to a convenient strength.

With the aid of the iodine solution the strength of which we now know exactly, and the solution of hyposulphite of soda which stands in a known relation to the same, we might make any determinations of iodine. The calculation, although in principle extremely simple, is yet somewhat hampered by reason of the long decimal which expresses the quantity of iodine in 1 c.c. of the solution. It is therefore convenient to dilute the iodine solution so that 1 c.c. may exactly contain ·005 grm. iodine. This is done by filling a litre flask therewith, and adding the necessary quantity of water; in our case 16·94 c.c., for 5 : 5·0847 :: 1000 : 1016·94. If the litre flask will hold above the mark this 16·94 c.c., it is simply added, otherwise it is put into the dry bottle destined to receive the iodine solution, the iodine solution added, the whole shaken together, a portion of the fluid returned to the flask, shaken, poured back into the bottle, and the whole shaken again.

The solution of hyposulphite may now be diluted in a corresponding manner. In our case we should have had to add 27·11 c.c. water to 1000 c.c. of the solution, as will be seen from the following consideration:—

20·2 c.c. of the original iodine solution correspond to 20 c.c. of the hyposulphite solution.

∴ 1000 c.c. correspond to 990·1 c.c.

Now these 1000 c.c. were made up to 1016·94 by addition of water; if therefore we make up 990·1 c.c. of the hyposulphite of soda to the same bulk by addition of water we shall have equivalent solutions. Hence, to 990·1 c.c. we must add 26·84 c.c. water, or to 1000 c.c. 27·11 water.

In such cases of dilution, I always prefer to take exactly 1 litre instead of an uneven number of c.c., as in measuring the latter errors and inaccuracies may readily occur; I have, therefore, above recommended the preparation of 1200 c.c. of the fluids, so that after their determination 1000 c.c. may be sure to remain.

c. THE ACTUAL ANALYSIS.

Weigh the iodine to be determined in the tubes fig. 96, dissolve it in iodide of potassium solution as in *b*, *β*, add hyposulphite solution from the burette till decoloration is just produced, then 3 or 4 c.c. starch solution, then iodine solution from a second burette to incipient blueness. The substance contains the same amount of iodine as the c.c. of iodine solution corresponding to the hyposulphite used *minus* the c.c. of the former used to destroy the excess of the latter. Where the solutions are of equal value and 1 c.c. corresponds to ·005 grm. iodine, the calculation is in the highest degree simple; for suppose we had used 21 c.c. NaO,S_2O_2 and 1 c.c. iodine, the quantity of iodine present is ·100 grm.

$$21 - 1 = 20, \text{ and } 20 \times \cdot 005 = \cdot 100$$

Where you are analysing chromic acid or peroxide of manganese by boiling with hydrochloric acid, and passing the chlorine evolved into iodide of potassium, you must allow the solution to cool before titrating with hyposulphite; for at a high temperature a portion of the tetrathionate of soda produced is converted into sulphate of soda by the iodine (WRIGHT*).

Free acid in the iodine solution to be estimated is not injurious; when such is present, however, the excess of the hyposulphite must be titrated without delay, or the free hyposulphurous may be decomposed before the iodine is added.

d. KEEPING OF THE SOLUTIONS.

The iodine solution and the hyposulphite solution are kept in glass-stoppered bottles in a cool, dark place. But the relation between the two solutions must be tested before each new series of experiments, and the iodine in the iodine solution must be redetermined.

If a fluid contains free iodine in presence of iodine in combination, determine the former in one portion by the combined method, and the total quantity in another portion. For this purpose you may either (1) add sulphurous acid to decoloration, precipitate with nitrate of silver (§ 145, I, *a*, *a*), digest the precipitate with nitric acid to remove any sulphite of silver which it may contain, filter, &c.; or (2) distil with sesquichloride of iron as directed, § 145, I. *b*, *ε*.

§ 147.

4. HYDROCYANIC ACID.†

I. *Determination.*

a. Gravimetric Estimation.—If you have free hydrocyanic acid in solution run it into an excess of solution of nitrate of silver, add a little nitric acid, allow to settle without warming, and determine the precipitated cyanide of silver either by collecting on a weighed filter, drying at 100° and weighing (§ 115, 3), or by collecting on an unweighed filter and converting into metallic silver. The latter operation is performed by igniting the precipitate in a porcelain crucible for ¼ hour, or till it ceases to lose weight (H. Rose). If you wish to determine in this way the hydrocyanic acid in bitter almond water or cherry laurel water, add ammonia after the addition of the solution of nitrate of silver till the fluid is strongly alkaline (it is not necessary to dissolve all the cyanide of silver) and *at once* acidify with nitric acid. When the precipitate has settled, filter. The whole of the cyanogen in the fluid will have been now converted into cyanide of silver. (The cyanogen was originally present partly as hydrocyanic acid, partly as cyanide of ammonium, but principally as hydrocyanate of benzaldehyd —S. Feldhaus*).

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* Zeitschr. f. anal. Chem. 9, 482.

† With regard to HERAPATH's colorimetric method, which is founded on the intensity of the color of a solution of persulphocyanide of iron, compare Chem. Gaz. Aug. 1853, 294.

Feldhaus recommends the following proportions: 100 grm. bitter almond water, about 1·2 grm. nitrate of silver dissolved in water and 2 to 3 c.c. ammonia sp. gr. ·96. A portion of the filtrate should be tested to make sure that it contains silver salt in excess, another portion should be tested by making it strongly alkaline with ammonia, and then acid again with nitric acid. If a precipitate is formed in the latter case it shows that the whole of the hydrocyanate of benzaldehyd was not decomposed, and the precipitation must be repeated. If you want to measure off a fluid containing hydrocyanic acid with a pipette, insert a little tube with soda-lime between the pipette and the flexible tube which you put into your mouth.

b. Liebig's *Volumetric Method* †—If hydrocyanic acid is mixed with potassa to strong alkaline reaction, and a dilute solution of nitrate of silver is then added, a permanent turbidity of cyanide of silver—or, if a few drops of solution of chloride of sodium have been added, of chloride of silver—forms only after the whole of the cyanogen is converted into double cyanide of silver and potassium. The first drop of solution of nitrate of silver added in excess produces the permanent precipitate. 1 eq. silver consumed in the process corresponds, therefore, exactly to 2 eq. hydrocyanic acid ($2KCy + AgO,NO_5 = AgCy,KCy + KO,NO_5$). A decinormal solution of nitrate of silver, containing consequently 10·793 grm. silver in the litre, should be used; 1 c.c. of this solution corresponds to ·005408 of hydrocyanic acid. In examining medicinal hydrocyanic acid, 5 to 10 grm. ought to be used, but of bitter almond water about 50 grm.; if exactly 5·408 or 54·08 grm. are used, the number of c.c. of the silver solution, divided by 10, or by 100, expresses exactly the percentage of hydrocyanic acid. Medicinal hydrocyanic acid is suitably diluted first by adding from 5 to 8 volumes of water; bitter almond water also is slightly diluted; if the latter is turbid the end-reaction will not be sufficiently distinct, and the gravimetric method is to be preferred.

Liebig has examined hydrocyanic acid of various degrees of dilution, and has obtained results by this method corresponding exactly with those obtained by *a.* Souchay,‡ too, obtained results almost identical; with pure dilute hydrocyanic acid, the gravimetric results were to the volumetric as 100 to 100·5—101; with clear or nearly clear bitter almond water as 100 to 102. Feldhaus (*loc. cit.*) obtained very nearly similar results. The slightly higher results of the volumetric process are to be explained from the fact that a small excess of silver solution is necessary to produce the final reaction. The less the amount of the substance taken the greater importance does this error assume. We should also notice that in the bitter almond water, which contains cyanide of ammonium, some ammonia is set free which has a solvent action on the cyanide of silver. In this method it does not matter whether the hydrocyanic acid contains an admixture of hydrochloric acid or formic acid. A considerable excess of potassa must be avoided.

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* Zeitschr. f. anal. Chem. 3, 34

† Annal. d. Chem. u Pharm. 77, 102.

‡ Zeitschr. f. anal. Chem. 2, 180.

If it is intended to determine cyanide of potassium by this method, a solution of that salt must be prepared of known strength, and a measured quantity used containing about ·1 grm. of the salt. Should it contain sulphide of potassium, a small quantity of freshly precipitated carbonate of lead must be first added, and the solution filtered before proceeding to the determination.

c. FORDOS *and* GELIS's *Volumetric Method.*[*] This method is founded upon the reaction of iodine upon cyanide of potassium :[†] $KCy + 2I = KI + ICy$. 2 eq. iodine = 253·7 correspond accordingly to 1 eq. cyanogen = 26·04, or to 1 eq. hydrocyanic acid = 27·04, or to 1 eq. cyanide of potassium = 65·17. The iodine solution is prepared according to the directions of § 146. If you have to examine free hydrocyanic acid, mix the fluid cautiously with solution of soda to alkaline reaction, add water containing carbonic acid (Seltzer or soda water), to convert a possible excess of alkali into bicarbonate (the fluid must not turn turmeric paper brown), and then iodine solution, until the fluid which was previously colorless becomes permanently yellowish. For the analysis of cyanide of potassium, prepare a fluid of known strength, and use a volume containing about ·05 of the salt; addition of carbonic acid water is necessary in the process. The cyanide must contain no sulphide of potassium. The method gives satisfactory results, see SOUCHAY (*loc. cit.*). It is not applicable to bitter almond water.

II. *Separation of Cyanogen from the Metals.*

a. In Cyanides of the Alkali Metals.

Mix the substance (if solid, without previous solution in water) with excess of nitrate of silver solution, then add water, finally nitric acid in slight excess, allow to settle without warming, and determine the cyanide of silver as in I., *a*. The bases are determined in the filtrate after separating the excess of silver.

b. In Cyanides and double Cyanides, which are completely decomposed by Nitrate of Silver and Nitric Acid or Nitrate of Silver and Ammonia.

Digest for some time with a dilute solution of nitrate of silver, stirring frequently,[‡] then add nitric acid in moderate excess, and digest at a gentle heat, till the foreign cyanide is fully dissolved and the cyanide of silver has become pure and quite white. Then add water and filter. As a precautionary measure it is well to test the metal obtained by long ignition of the cyanide of silver, whether it is free from those metals which were combined with the cyanogen. The filtrate is used for estimating the bases, the silver being first precipitated with hydrochloric acid. This method affords us an exact analysis of the double cyanides of potassium with nickel, copper and zinc (H. **Rose**).

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[*] Journ. de Chim. et de Pharm. 23, 48.

[†] Mentioned first by SERULLAS and WÖHLER.

[‡] Double cyanide of nickel and potassium yields by this process a mixture of cyanide of silver with cyanide of nickel. Like double cyanides are similarly decomposed.

W. **Weith**[*] recommends a solution of nitrate of silver in ammonia for the decomposition of many cyanogen compounds, such as ferrocyanide of potassium, Prussian blue, and even cobalticyanide of potassium. He digests them in sealed tubes at 100° (in the case of cobalticyanide of potassium, 150°) for 4 or 5 hours. Warm the contents of the tube gently in a dish, until the crystals of ammonio-cyanide of silver are dissolved, filter off the separated metallic oxide, wash it with ammonia, dilute, and precipitate the cyanide of silver by acidifying with nitric acid. In the filtrate separate the silver from the alkalies, &c. In respect to the undissolved oxides it should be noted that metallic silver is always mixed with the oxide of iron.

c. In Cyanide of Mercury.

Precipitate the aqueous solution with sulphuretted hydrogen; the sulphide of mercury may be filtered without difficulty if a little ammonia or hydrochloric acid be added; it is determined according to § 118, 3. If the compound is in the solid condition, the cyanogen may be determined in another portion by ignition with oxide of copper, the nitrogen and carbonic acid being collected and separated (comp. Organic Analysis).

H. **Rose** and **Finkener**[†] have, after much trouble, succeeded in finding out a method for determining cyanogen with precision also in solutions of cyanide of mercury. Mix the solution of the cyanide of mercury with nitrate of zinc dissolved in ammonia. To 1 part of mercury-salt you may add about 2 parts of the zinc-salt. Add to the clear solution sulphuretted hydrogen water gradually till it produces a perfectly white precipitate of sulphide of zinc. The precipitate, which is a mixture of the sulphides of mercury and zinc, settles well. After a quarter of an hour filter it off and wash with very dilute ammonia. The filtrate contains cyanide of zinc dissolved in ammonia, together with nitrate of ammonia. It does not smell of hydrocyanic acid, and consequently no escape of the latter takes place. Mix it with nitrate of silver and then add dilute sulphuric acid in excess. The cyanide of silver is next washed a little by decantation, then—to free it from any cyanide of zinc simultaneously precipitated—heated with a solution of nitrate of silver, finally filtered off, washed, and determined after I., *a*. The precipitated sulphides may be dissolved in aqua regia, and the mercury precipitated as subchloride according to § 118, 2. The test-analyses communicated by **Rose** yielded excellent results.

d. In compounds decomposable by Oxide of Mercury in the Wet Way.

Many simple cyanides, and also double cyanides—both of the character of the double cyanide of nickel and potassium, and of the ferro- or ferricyanides (not, however, cobalticyanides)—may, as is well known, be completely decomposed by boiling with excess of oxide of mercury and water, all cyanogen being obtained as cyanide of mercury, and the metals passing into oxides.

H. **Rose** (*loc. cit.*) has shown that Prussian blue, ferro- and ferricyanide of potassium, more particularly, may be readily analysed in this manner.

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[*] Zeitschr. f. anal. Chem. 9, 379.

[†] *Ib.* 1, 288.

Boil a few minutes with water and *excess* of oxide of mercury till complete decomposition is effected, add—in order to render the sesquioxide of iron and oxide of mercury removable by the filter—nitric acid in small portions, till the alkaline reaction has nearly disappeared, filter, wash with hot water, dry the precipitate, ignite—very gradually raising the heat—under a hood (with a good draught), and weigh the sesquioxide of iron remaining. In the filtrate the cyanogen is determined according to *c*, and any potassa that may be present is estimated in the filtrate from the cyanide of silver.

e. Determination of Metals contained in Cyanides with decomposition and volatilization of the Cyanogen.

Of the various means for completely decomposing compounds of cyanogen, especially also the double cyanides, according to H. Rose (*loc. cit.*) three particularly are worthy of recommendation—viz., concentrated sulphuric acid, sulphate of mercury, and chloride of ammonium. The nitrates seemed decidedly less suitable on account of their too violent action.

α. Decomposition by Sulphuric Acid. All cyanogen compounds, simple or double, are completely decomposed and converted into sulphates or oxides, as the case may be, if treated in a powdered condition in a platinum dish or a capacious platinum crucible with a mixture of about 3 parts concentrated sulphuric acid and 1 part water, and heated till almost all the sulphuric acid has been expelled. The residual mass is then free from cyanogen. It is dissolved in water, if necessary with addition of hydrochloric acid, and the oxides determined by the usual methods. This way is not adapted for cyanide of mercury, as a little of the metal would escape with the fumes of the sulphuric acid.

β. Decomposition by Sulphate of Mercury. Of the combinations of oxide of mercury with sulphuric acid, those suitable to our present purpose are the neutral and the basic (Turpeth mineral). The substance is mixed with 6 parts of the latter, heated in a platinum crucible gradually, and finally maintained for a long time at a red-heat, till all the mercury has volatilized, and the weight of the crucible remains constant. If alkalies are present, a little carbonate of ammonia is added during the final ignition, from time to time, in order to convert the bisulphates into neutral salts. The residue may usually be analysed by simple treatment with water; in the case of ferrocyanide of potassium, for instance, the sulphate of potassa dissolves and pure (alkali-free) sesquioxide of iron remains behind. The test-analyses that have been communicated yielded excellent results.

γ. Decomposition by Chloride of Ammonium. Mix the substance with twice or thrice the amount of this salt and ignite the mixture moderately in a stream of hydrogen (apparatus, p. 200, fig. 79). From the cooled mass water extracts alkaline chloride, while the reducible metals remain in the metallic state. The method is peculiarly adapted for the analysis of double cyanide of nickel and potassium and cobalti-cyanide of potassium, not so for iron compounds, since the iron obtained is not pure, but contains carbon.

If one of the methods described in *e* is employed, the nitrogen and carbon (the cyanogen) must be determined by a combustion, if an estimation by the loss is not sufficient.

f. Determination of the Alkalies, especially of Ammonia in Soluble Ferrocyanides.

Mix the boiling solution with a solution of chloride of copper, in moderate excess, filter off the precipitated ferrocyanide of copper, free the filtrate from copper by means of sulphuretted hydrogen, and then determine the alkalies (REINDEL*). For fixed alkalies, you may also ignite with hyposulphite of baryta (FRÖHDE†).

g. Volumetric Determination of Ferro- and Ferricyanogen.

a. After E. DE HAEN. This method devised in my laboratory, is founded upon the simple fact that a solution of ferrocyanide of potassium acidified with sulphuric acid (and which may accordingly be assumed to contain free hydroferrocyanic acid), is by addition of permanganate of potassa converted into the corresponding ferricyanide. If this conversion is effected in a very dilute fluid, containing about ·2 grm. ferrocyanide of potassium in from 100 to 200 c.c., the termination of the reaction is clearly and unmistakably indicated by the change of the originally pure yellow color of the fluid to reddish-yellow.‡

The process requires two test fluids of known strength, viz.—

1. A solution of pure ferrocyanide of potassium.
2. A solution of permanganate of potassa.

The *former* is prepared by dissolving 20 grm. perfectly pure and dry crystallized ferrocyanide of potassium in water to 1 litre; each c.c. therefore contains 20 mgrm. The *latter* is diluted so that somewhat less than a buretteful is required for 10 c.c. of the solution of ferrocyanide of potassium.

To determine the strength of the permanganate of potassa solution in its action upon the ferrocyanide of potassium, measure off, by means of a pipette, 10 c.c. of the solution of ferrocyanide of potassium (containing ·2 grm.), dilute with 100 to 200 c.c. water, acidify with sulphuric acid, place the glass on a sheet of white paper, and allow the permanganate to drop into the fluid, stirring it at the same time, until the change from yellow to *reddish*-yellow indicates that the conversion is complete.§ Repetitions of the experiment always give very accurately corresponding results. If at any time you have reason to suspect that the permanganate has suffered alteration, recourse must be had again to this experiment. If after acidifying the ferrocyanide of potassium with sulphuric acid you add a trace of sesquichloride of iron to produce a bluish-green color, the latter will disappear at the end of the reaction, which is thus rendered very distinct, (GINTL‖)

To determine the amount of real ferrocyanide of potassium contained in any given sample of the commercial article, dissolve 5 grm. to 250 c.c.; take 10 c.c. of this solution, and examine as just directed. Suppose, in determining the strength of the permanganate, you have used 20 c.c., and you find now that 19 c.c. is sufficient, the simple rule of three sum,

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* Journ. f. prakt. Chem. 65, 452.

† Zeitschr. f. anal. Chem. 3, 181.

‡ Instead of the permanganate you may use chromate of potash. The solution is added till spots of sesquichloride of iron on a plate are no longer colored blue or green, but brownish. E. MEYER, Zeitschr. f. anal. Chem. 8, 508.

§ If you wish at first for some additional evidence besides the change of color, add to a drop of the mixture on a plate, a drop of solution of sesquichloride of iron: if this fails to produce a blue tint, the conversion is accomplished.

‖ Zeitschr. f. anal. Chem. 6, 446.

$$20 : \cdot 2 :: 19 : x$$

will inform you how much pure ferrocyanide of potassium ·2 grm. of the analysed salt contains. And even this small calculation may be dispensed with, by diluting the permanganate so that exactly 50 c.c. correspond to ·2 of ferrocyanide of potassium, as, in that case, the number of half-c.c. consumed expresses directly the percentage of pure ferrocyanide.

Instead of determining the strength of the permanganate by means of pure ferrocyanide of potassium, which is unquestionably the best way, one of the methods given in § 112, 2, may also be employed; bearing in mind, in that case, that 2 eq. ferrocyanide of potassium = 442·76, 2 eq. iron dissolved to protoxide = 56, and 1 eq. oxalic acid = 63 are equivalent in their action upon solution of permanganate of potassa.

The analysis of soluble ferricyanides by this method is effected by reducing them to ferrocyanides, acidifying, and then proceeding in the way described. The reduction is effected as follows:—Mix the weighed ferricyanide with a solution of soda or potassa in excess, boil, and add concentrated solution of sulphate of protoxide of iron gradually, and in small portions, until the color of the precipitate appears black, which is a sign that protosesquioxide of iron has precipitated. Dilute now to 300 c.c., mix, filter, and proceed to determine the ferrocyanide in portions of 50 or 100 c.c. of the fluid. As the space occupied by the precipitate is not taken into account in this process, the results are not absolutely accurate; the difference is so very trifling, however, that it may safely be disregarded. GINTL (*loc. cit.*) suggests to put the neutral or alkaline fluid in a tall vessel and add a few lumps of sodium amalgam as big as peas: in ten minutes the reduction will be effected and without the aid of heat.

Insoluble ferro- or ferricyanides, decomposable by boiling solution of potassa (as are most of these compounds), are analysed by boiling a weighed sample sufficiently long with an excess of solution of potassa (adding, in the case of ferricyanides, sulphate of protoxide of iron), and then proceeding as directed above.

β. After E. LENSSEN.

Ferricyanides may be analysed also by another method, also devised in my laboratory. It is founded on the fact that, when ferricyanide of potassium, solution of iodide of potassium, and concentrated hydrochloric acid are mixed together, 1 eq. iodine (126·85) separates for every eq. ferricyanide of potassium (329·63) : $H_3Cfdy + HI = 2H_2Cfy + I$. By determining the liberated iodine according to § 146, we learn the quantity of the ferricyanide of potassium. LENSSEN obtained in 4 experiments respectively, 99·22,—101·7,—102·1,—100·5, instead of 100. The fluid should not be diluted till after the addition of hydrochloric acid. C. MOHR* obtained still more accurate results, as he avoided the formation of hydroferrocyanic acid by adding solution of sulphate of zinc, thus obtaining, instead of the former, ferrocyanide of zinc, which is not in the least decomposed by iodine. He directs to mix the dilute solution of the ferricyanide of potassium with iodide of potassium and hydrochloric acid in excess, add an excess of iron-free sulphate of zinc solution, neutralize the free acid with bicarbonate of soda added in slight excess, and determine the separated iodine according to § 146.

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* Annal. d. Chem. u. Pharm. 105, 62.

γ. To the estimation of ferrocyanogen in dyers' baths, which contain oxidizable organic matter, H. RHEINECK[*] applies the fact that when solution of sesquioxide of iron is gradually added to ferrocyanide of potassium, no matter whether a mineral acid is present or not, at first a clear blue fluid is produced, which becomes afterwards turbid, and when all the ferrocyanogen is exactly thrown down a flocculent precipitate of Prussian blue appears suspended in a clear colorless fluid. A certain measure of the bath is taken, and the same measure of a standard solution of ferrocyanide of potassium; to these are added a solution of sesquichloride of iron from a burette till the flocculent precipitate separates. The calculation is sufficiently obvious.

δ. After E. BOHLIG.[†]

In the case of a fluid containing ferrocyanide of potassium, and also sulphocyanide (for instance, the red liquor of the prussiate works), the method given in *a* cannot be employed, as the hydrosulphocyanic acid also reduces permanganic acid. The following method—depending on the precipitation of the ferrocyanogen with solution of sulphate of copper —may then be used; it is accurate enough for technical purposes. Dissolve 10 grm. pure sulphate of copper to 1 litre, also 4 grm. pure dry ferrocyanide of potassium to 1 litre. Add to 50 c.c. of the latter solution (which contain ·2 grm. ferrocyanide of potassium) copper solution from a burette to complete precipitation of the ferrocyanogen. In order to hit this point exactly, from time to time dip a strip of filter-paper into the brownish-red fluid which will imbibe the clear filtrate, leaving the precipitate of ferrocyanide of copper behind. At first the moist strips of paper, when touched with sesquichloride of iron, become dark blue, the reaction gradually gets weaker and weaker, and finally vanishes altogether. We now know the value of the copper solution with reference to its action on ferrocyanide of potassium, and can, therefore, by its means test solutions containing unknown amounts of ferrocyanogen. If alkaline sulphides are present, they are first removed by boiling with carbonate of lead. After filtering off the sulphide of lead, acidify with dilute sulphuric acid, and then proceed.

§ 148.

5. HYDROSULPHURIC ACID.

I. *Determination.*

To determine sulphuretted hydrogen *in a mixture of gases* confined over mercury[‡] it may be absorbed by a ball made of 2 parts precipitated phosphate of lead and 3 parts plaster of Paris. The mixture is made into a paste with water, and pressed into a bullet mould in which the platinum wire is inserted. The mould should previously be oiled. The balls are dried at 100°, saturated with concentrated phosphoric acid, and are then ready for use (LUDWIG[§]).

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[*] Chem. Centralbl. 1871, 778

[†] Polytechn. Notizblatt, 16, 81.

[‡] When this gas remains long in contact with mercury, sulphide of mercury is liable to be formed.

[§] Annal. d. Chem. u. Pharm. 162, 55.

To determine sulphuretted hydrogen *dissolved in water* the following methods are in use:—

a. The method of determining sulphuretted hydrogen volumetrically by solution of iodine, was employed first by DUPASQUIER; it is very convenient and accurate. That chemist used alcoholic solution of iodine. But as the action of the iodine upon the alcohol alters the composition of this solution somewhat rapidly, it is better to use a solution of iodine in iodide of potassium. The decomposition is as follows:—

$$\mathrm{HS} + \mathrm{I} = \mathrm{HI} + \mathrm{S}$$

1 eq. $\mathrm{I} = 126{\cdot}85$ corresponds, therefore, to 1 eq. $\mathrm{HS} = 17$. However, this exact decomposition can be relied upon with certainty only if the amount of sulphuretted hydrogen in the fluid does not exceed ·04 per cent. (BUNSEN). Fluids containing a larger proportion of sulphuretted hydrogen must therefore first be diluted to the required degree with boiled water cooled out of the contact of air.

The iodine solution of § 146 may be used for the estimation of larger quantities of sulphuretted hydrogen; for weak solutions, *e.g.*, sulphuretted mineral water, it is advisable to dilute the iodine solution 5 times, so that 1 c.c may contain ·001 grm. iodine.

The process is conducted as follows:—

Measure or weigh a certain quantity of the sulphuretted water, dilute, if required, in the manner directed, add some thin starch-paste, and then solution of iodine, with constant shaking or stirring, until the permanent blue color begins to appear. The result of this experiment indicates approximately, but not with positive accuracy, the relation between the examined water and the iodine solution. Suppose you have consumed, to 220 c.c. of the sulphuretted water, 12 c.c. of a solution of iodine containing ·000918 grm. iodine in the c.c.[*] Introduce now into a flask nearly the quantity of iodine solution required, add the sulphuretted water in quantity either already determined, or to be determined, by weight or measure;[†] then to the colorless fluid add thin starch-paste, and after this iodine solution until the blue color just begins to show. By this course of proceeding, you avoid the loss of sulphuretted hydrogen which would otherwise be caused by evaporation and oxidation. In my analysis of the Weilbach water, 256 c.c. of the water required, in my second experiment, 16·26 c.c. of iodine solution, which, calculated to the quantity of sulphuretted water used in the first experiment, viz., 220 c.c., makes 13·9 c.c., or 1·9 c.c. more. But even now the experiment cannot yet be considered quite conclusive, when made with a solution of iodine so dilute; it being still necessary to ascertain how much iodine solution is required to impart the same blue tint to the same quantity of ordinary water mixed with starch-paste, of the same temperature,[‡] and as nearly as possible in the same condition[§] as the analysed sulphuretted water, and to deduct this from the quantity of iodine solution used in the second experiment. Thus in the case mentioned, I had to deduct ·5 c.c. from the 16·26 c.c. used. If the instructions here given are strictly followed, this method gives very accurate results (see Expt. No. 82).

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[*] The numbers here stated are those which I obtained in the analysis of the Weilbach water.

[†] Compare Experiment, No. 82. [‡] Annal. d. Chem. u. Pharm. 102, 186.

[§] In this connexion I would recommend, in cases where the sulphuretted water contains bicarbonate of soda, to add to the ordinary water an equal quantity of this salt, as its presence has a slight influence on the appearance of the final reaction.

b. **Fr. Mohr's** method, slightly modified.

Mix the sulphuretted fluid with a slight excess of solution of arsenite of soda of known strength (determined by means of iodine solution, see § 127, 5, *a*), and add hydrochloric acid to distinct acid reaction. Dilute to 300 c.c., pass through a dry filter, test a sample of the filtrate with sulphuretted hydrogen, to make quite sure that it still contains arsenious acid, and then determine in 100 c c., after addition of powdered bicarbonate of soda, the remainder of the arsenious acid left in it. Deduct the quantity of iodine solution consumed in the last part of the process, multiplied by 3 (as only 100 of the 300 c.c. have been operated upon), from that which corresponds to the entire quantity of arsenious acid used in the process: the remainder expresses the quantity of iodine solution corresponding to the sulphuretted hydrogen present. In making the calculation, bear in mind that 2 eq. iodine here correspond to 3 eq. HS, since 1 eq. AsO_3 decomposes, on the one hand, 3HS, producing AsS_3 and 3HO, and requires, on the other hand, 2 eq. iodine for its conversion into arsenic acid.

Very dilute solutions of sulphuretted hydrogen cannot be analysed by this method, as the sulphide of arsenic separating from them takes a long time to deposit, and a minute portion of it invariably remains in solution.*

c. Mix the sulphuretted fluid with an excess of solution of arsenite of soda, add hydrochloric acid, allow to deposit, and determine the sulphide of arsenic as directed § 127, 4. If the quantity of sulphuretted hydrogen present is moderately large, the results are accurate (compare Expt. No. 82); but in the case of very dilute solutions, the results are too low, as a little tersulphide of arsenic remains in solution. Hence, in my analysis of the Weilbach water, this method gave only ·006621 and ·006604 per 1000, whilst water taken from the well at the same time, and titrated with iodine, gave ·007025. Instead of arsenious acid, solution of acetate of copper and acetic acid or solution of silver may be employed as precipitant, and the sulphur determined in the sulphide of copper as sulphate of baryta (see II.), or in the sulphide of silver as metallic silver. The results obtained with acetate of copper are also too low, in the case of very dilute fluids. As regards precipitation by silver solution, I cannot yet speak from actual experience. **Lyte**† recommends solution of chloride of silver in hyposulphite of soda, mixed with a few drops of ammonia, as the most suitable for the purpose. In analysing a water containing sulphate of iron, **Lyte**‡ threw down the sulphuretted hydrogen with freshly precipitated sulphate of lead, filtered off, washed, extracted the sulphate of lead with hot solution of acetate of ammonia, converted the residual sulphide into sulphate, and weighed the latter.

For the analysis of mineral waters, the method *a* will always answer best, unless presence of hyposulphites should impair its accuracy.

d. If the sulphuretted hydrogen is evolved in the gaseous state, and large quantities are to be determined, the best way is to conduct it first through several bulbed U-tubes (fig. 95, p. 361), containing an alkaline solution of arsenite of soda, then through a tube connected with the exit of the last U-tube, which contains pieces of glass moistened with solution of soda; to mix the fluids afterwards, and proceed as in *b* or *c*. If, on the other hand, we have to determine small quantities of sulphuretted hydrogen contained in a large amount of air, &c., it is well to pass the gaseous mixture in separate small bubbles through a very dilute solution of iodine in iodide of potassium, of known volume and strength, which is contained in a long glass tube fixed in an inclined position and protected against sunlight. The free iodine remaining is finally estimated by means of a solution of hyposulphite of soda (§ 146); the difference gives us the quantity of iodine which has been converted by sulphuretted hydrogen into hydriodic acid, and consequently corresponds to the amount of the sulphuretted hydrogen present. The volume of the gaseous mixture may be known by measuring the water which has escaped from the aspirator used. The arrangement of the absorption tube is the same as is figured in connexion with the Determination of Carbonic Acid in the Air. The thin glass tube conducting the gas into the absorption tube, however, must not be provided with an india-rubber elongation.

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* A solution containing in the litre ·003 HS did not give with a solution of arsenious acid in hydrochloric acid, a precipitate admitting of filtration till after a lapse of twelve hours.

† Comp. rend. 43, 765. ‡ Zeitschr. f. anal. Chem. 5, 441.

From my own experiments* it appears that sulphuretted hydrogen whether in small or large quantities may be also estimated by the increase in weight of absorption tubes. We have only to take care that the mixture of gases is first thoroughly dried by passing over chloride of calcium. To take up the sulphuretted hydrogen we use U-tubes, five-sixths filled with sulphate of copper on pumice, one-sixth at the exit containing chloride of calcium. To prepare the pumice with sulphate of copper, proceed as follows. Treat 60 grm. pumice in lumps the size of peas in a small porcelain dish with a hot concentrated solution of 30 or 35 grm. sulphate of copper, dry the whole with constant stirring, place the dish in an air or oil bath of the temperature of 150° to 160°, and allow to remain therein four hours. A tube containing 14 grm. of this prepared pumice will absorb about ·2 grm. sulphuretted hydrogen. It is well always to employ two such tubes. If the prepared pumice is dried at a lower temperature it takes up much less of the gas, if dried at a higher temperature the gas is decomposed and sulphurous acid is formed. This method is more completely given under the Analysis of Black Ash.

Finally, small quantities of sulphuretted hydrogen mixed with other gases may be estimated by passing through bromine water and converting into sulphuric acid (compare II., A. 2).

II. *Separation and Determination of Sulphur in Sulphides.*

A. METHODS BASED ON THE CONVERSION OF THE SULPHUR INTO SULPHURIC ACID.

1. *Methods in the Dry Way.*

a. Oxidation by Alkaline Nitrates (applicable to all compounds of sulphur). If the sulphides do not lose any sulphur on heating, mix the pulverized and weighed substance with 6 parts of anhydrous carbonate of soda and 4 of nitrate of potassa, with the aid of a rounded glass rod, wipe the particles of the mixture which adhere to the rod carefully off against some carbonate of soda, and add this to the mixture. Heat in a platinum or porcelain crucible (which, however, is somewhat affected by the process), at a gradually increased temperature to fusion;* keep the mass in that state for some time, then allow it to cool, heat the residue with water, filter the fluid, boil the residue with a solution of pure carbonate of soda, filter, wash, remove all nitric acid from the filtrate by repeated evaporation with pure hydrochloric acid, and determine the sulphuric acid as directed in § 132. The metal, metallic oxide, or carbonate, which remains undissolved, is determined, according to circumstances, either by direct weighing or in some other suitable way. In the presence of lead, before filtering, pass carbonic acid through the solution of the fused mass, to precipitate the small quantity of that metal which has passed into the alkaline solution.

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* Zeitschr. f. anal. Chem. 10, 75.

Should the sulphides, on the contrary, lose sulphur on heating, the finely powdered compound is mixed with 4 parts carbonate of soda, 8 parts nitre, and 24 parts pure and perfectly dry chloride of sodium, and the process otherwise conducted as already given.

b. Oxidation by Chlorate of Potassa. The oxidation of sulphides by a mixture of chlorate of potassa and carbonate of soda has been repeatedly recommended. There is this advantage in connexion with it, viz., that the sulphuric acid in the fused mass may be more readily converted into pure sulphate of baryta than when nitrates are present; on the other hand,—at least with the proportions usually recommended: 1 part sulphide, 3 parts chlorate of potassa, and 3 parts carbonate of soda (or 4 parts mixed carbonates)—the process is attended with the inconvenience that many sulphides, *e.g.*, fahlerz and sulphide of antimony, occasion very violent explosions.† Also, with many sulphides, *e.g.*, iron and copper pyrites, the decomposition is not complete (FR. MOHR). In these two respects therefore we must be cautious in the use of this method. H. ROSE recommends 6 or 8 parts carbonate of soda and 1 part chlorate of potash for 1 part of substance.

c. Oxidation by Chlorine Gas (after BERZELIUS and H. ROSE, especially suitable for sulphosalts of complicated composition).

The following apparatus, or one of similar construction, is used; corks should be used, not india-rubber stoppers, and wherever there is an india-rubber connexion, the glass tubes should be close to each other.

A is the evolution flask,‡ *B* contains concentrated sulphuric acid, *C* chloride of calcium. *D* contains the substance; the straight tube should be rather narrow, and inclined slightly to prevent the heavy fumes from returning. *E* is the receiver containing water (or—in the presence of antimony—solution of tartaric acid in dilute hydrochloric acid), *F* is a U-tube also containing water, *G* conducts the escaping chlorine into a carboy filled with moist hydrate of lime.

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* If the coal gas contains sulphur, some is likely to be absorbed by the fusion—PRICE, Journ. Chem. Soc. (2) 2, 51. If a platinum crucible is used, do not raise the heat more than necessary, or the crucible may be attacked.

† Annal. d. Chem. u. Pharm. 107, 128.

‡ Pour a *perfectly cold* mixture of 45 parts of sulphuric acid and 21 of water, over one of 18 parts of chloride of sodium and 15 of *finely powdered* binoxide of manganese, and shake, when a steady evolution of chlorine will at once begin, which, when it shows signs of slackening, may be promoted by a *gentle* heat.

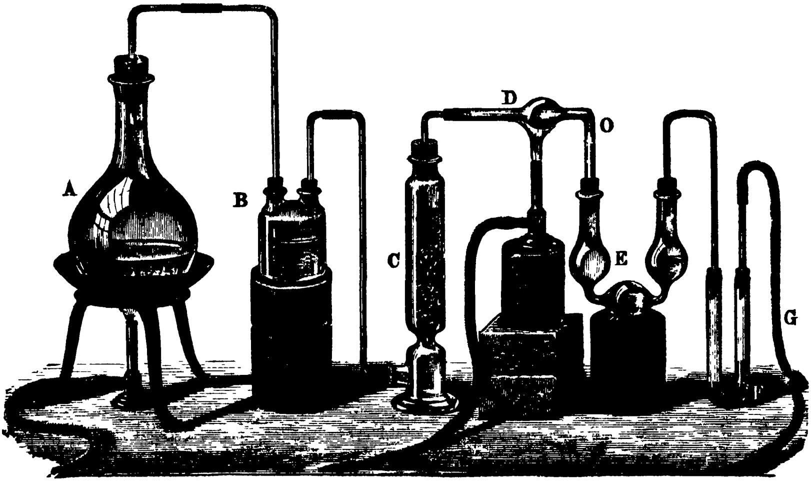

Fig. 97.

When the apparatus is arranged, the sulphide to be examined is weighed in a narrow glass tube sealed at one end, and subsequently cautiously transferred from this tube to the bulb, in the manner illustrated by fig. 98, so as to prevent any portion of the substance getting into the ends of the bulb-tube.

When the apparatus is filled with chlorine, *D* is connected with *C*, and the chlorine is allowed to act on the sulphide, at first without the aid of heat. When no further alteration is observed—the receiver *E* being full of chlorine—a very gentle heat is applied to the bulb, care being taken also to keep the tube *O* warm, securing it thus from being stopped up by the sublimate of a volatile chloride. The sulphide is completely decomposed by the chlorine, the metals being converted into chlorides, which partly remain in the bulb, partly—(viz., the volatile ones, as chloride of antimony, chloride of arsenic, chloride of mercury)—pass over into the receiver; the sulphur combines with the chlorine to chloride of sulphur, which passes into *E*, where, coming in contact with water it decomposes with the latter, forming hydrochloric acid and hyposulphurous acid, with separation of sulphur. The hyposulphurous acid decomposes again into sulphur and sulphurous acid, which latter is at last, by the action of the chlorine water in *E*, converted into sulphuric acid. The final result of the decomposition is consequently sulphuric acid and a greater or less amount of separated sulphur. The separation of sulphur is troublesome, and may be avoided to a certain extent by heating slowly. The operation is con-

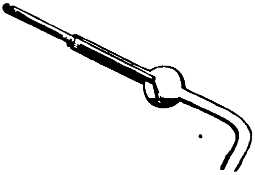

Fig. 98.

cluded when no more products—with the exception, perhaps, of sesquichloride of iron, the complete expulsion of which need not be awaited—pass over from the bulb. Heat is then applied to the bulb-tube, proceeding from the bulb towards the bend, so as to force all the chloride of sulphur and the volatile metallic chlorides to pass over into *E*, or at least to occupy the end of the bulb-tube.

The apparatus is left undisturbed a short time longer, after which the tube is cut off under the bend at *O*, and the separated end, which generally contains a portion of the volatile chlorides, closed with a smooth cork or by inverting over it a glass-tube sealed at one end and moistened inside. The whole is now allowed to stand 24 hours, to allow the volatile chlorides to absorb moisture, which will render them soluble in water without generating heat. The metallic chlorides in the cut-off end of the tube are then dissolved in dilute hydrochloric acid, the end is rinsed, and the solution added to the contents of the tubes *E* and *F*; a very gentle heat is now applied until the free chlorine is expelled, and the fluid is then allowed to stand until the sulphur has solidified. The sulphur is filtered off on a weighed filter, washed, dried, and weighed. The filtrate is precipitated with chloride of barium (§ 132), by which operation the amount of that portion of the sulphur is determined which has been converted into sulphuric acid. The fluid filtered from the sulphate of baryta contains, besides the excess of chloride of barium added, also the volatile metallic chlorides; which latter are finally determined in it by the proper methods, which will be found in Section V.

The chloride remaining in the bulb-tube is either at once weighed as such (chloride of silver, chloride of lead), or where this is impracticable—as in the case of copper, for instance, which remains partly as subchloride partly as chloride—it is dissolved in water, hydrochloric acid, nitrohydrochloric acid, or some other suitable solvent, and the metal or metals in the solution are determined by the methods already described, or which will be found in Section V. To be enabled to ascertain the weight of the bulb-tube containing chloride of silver, it is advisable to reduce the chloride by hydrogen gas, and then dissolve the metal in nitric acid.

In cases where you have only to estimate the sulphur, say in substances containing also sulphuric acid, O. LINDT* recommends conducting the chloride of sulphur and the volatile metallic chlorides into pure solution of soda, when decomposition immediately takes place, producing sulphide of sodium, hyposulphite of soda, chloride of sodium, and hypochlorite of soda. When the decomposition is over, continue passing the chlorine for two hours through the soda, evaporate then to dryness, ignite the residue cautiously to destroy the chlorate of soda, dissolve in water, and estimate the sulphuric acid according to § 132.

d. Oxidation by Oxide of Mercury (*after* BUNSEN).

This method, which will be found in detail, § 188, is particularly suited to the estimation of sulphur in volatile compounds, or in substances which when heated lose sulphur.

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* Zeitschr. f. anal. Chem. 4, 370.

2. *Methods in the Wet Way.*

a. Oxidation of the Sulphur by Acids yielding Oxygen, or by Halogens.[*]

a. Weigh the finely pulverized sulphide in a small glass tube sealed at one end, and drop the tube into a tolerably capacious strong bottle with glass stopper, which contains red fuming nitric acid (perfectly free from sulphuric acid†) in more than sufficient quantity to effect the decomposition of the sulphide. Immediately after having dropped in the tube, close the bottle. When the action, which is very impetuous at first, has somewhat abated, shake the bottle a little; as soon as this operation ceases to cause renewed action, and the fumes in the flask have condensed, take out the stopper, rinse this with a little nitric acid into the bottle, and then heat the latter gently.

aa. The whole of the Sulphur has been oxidized, the Fluid is perfectly clear:‡ Evaporate with some chloride of sodium, towards the end adding pure hydrochloric acid repeatedly, cooling the dish each time before adding the acid. Dilute with much water, and determine the sulphuric acid as directed § 132. Make sure that the precipitate is pure, if it is not purify it according to § 132. Separate the bases in the filtrate from the excess of the salt of baryta by the methods given in Section V.

bb. Undissolved Sulphur floats in the Fluid: Add chlorate of potassa in small portions, or strong hydrochloric acid, and digest some time on a water-bath. This process will often succeed in dissolving the whole of the sulphur. Should this not be the case, and the undissolved sulphur appear of a pure yellow color, dilute with water, collect on a weighed filter, wash carefully, dry, and weigh. After weighing, ignite the whole, or a portion of it, to ascertain whether it is perfectly pure. If a fixed residue remains (consisting commonly of quartz, gangue, &c., but possibly also of sulphate of lead, sulphate of baryta, &c.), deduct its weight from that of the impure sulphur. In the filtered fluid determine the sulphuric acid as in *aa*, calculate the sulphur in it, and add the amount to that of the undissolved sulphur. If the residue left upon the ignition of the undissolved sulphur contains an insoluble sulphate, decompose this as directed in § 132, and add the sulphur found in it to the principal amount.

In the presence of bismuth, the addition of chlorate of potassa or of hydrochloric acid is not advisable, as chlorine interferes with the determination of bismuth.

β. Mix the finely pulverized metallic sulphide in a dry flask, by shaking, with powdered chlorate of potassa (free from sulphuric acid), and add moderately concentrated hydrochloric acid in small portions. Cover the flask with a watch-glass, or with an inverted small flask. After digestion in the cold for some time, heat gently.

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[*] In presence of lead, baryta, strontia, lime, tin, and antimony, method *b* is preferable to *a*.

† To test for sulphuric acid in nitric or hydrochloric acid, it is necessary to evaporate on a water-bath nearly to dryness and take up with water before adding chloride of barium. When the acid cannot be got pure, determine the sulphuric acid and allow for it.

‡ This can of course be the case only in absence of metals forming insoluble salts with sulphuric acid. If such metals are present, proceed as in *bb*, as it is in that case less easy to judge whether complete oxidation of the sulphur has been attained.

finally on the water-bath, until the fluid smells no longer of chlorine. Proceed now as directed in *a*, *aa*, or *bb*, according as the sulphur is completely dissolved or not. In the latter case you must of course immediately dilute and filter. The oxidation of the sulphur may be usually effected more quickly and completely by warming with nitric acid of 1·36 sp. gr. on a water-bath, and adding chlorate of potash in small portions. Compare STORER,* PEARSON, and BOWDITCH.†

γ. Aqua regia is also frequently used. J. LEFORT‡ recommends a mixture of 1 part strong hydrochloric acid, and 3 parts strongest nitric acid.

δ. Bromine may also be used. Pyrites or blende is digested at a gentle heat with water, and bromine gradually added. If the sulphides have been prepared in the wet way, good bromine water is sufficient to oxidize them. P. WAAGE§ prefers bromine to all other wet agents, and advises its purification by distillation in an apparatus from which all caoutchouc connexions are excluded.

b. Oxidation of the Sulphur by Chlorine in Alkaline Solution, after RIVOT, BEUDANT, *and* DAGUIN.‖ (Suitable also for determining the sulphur in the crude article).

Heat the very finely pulverized sulphide or crude sulphur, for several hours with solution of potassa free from sulphuric acid (which dissolves free sulphur, as well as the sulphides of arsenic and antimony), and then conduct chlorine into the fluid. This speedily oxidizes the sulphur; the sulphuric acid formed combines with the potassa to sulphate, which dissolves in the fluid, whilst the metals converted into oxides remain undissolved. Filter, acidify the alkaline filtrate, and precipitate the sulphuric acid by chloride of barium (§ 132). Arsenic and antimony pass into the alkaline solution in the form of acids, but not so lead, which is converted into binoxide, and remains completely undissolved. This method is, therefore, particularly suitable in presence of sulphide of lead. In presence of sulphide of iron, sulphate of potassa is formed at first, and hydrate of sesquioxide of iron, which, if the action of the chlorine is allowed to continue, begins to be converted into ferrate of potassa. As soon, therefore, as the fluid commences to acquire a red tint, the transmission of chlorine must be discontinued, and the fluid gently heated for a few moments with powdered quartz, to decompose the ferric acid.

It occasionally happens, more particularly in presence of sand, iron pyrites, oxide of copper, &c, that the process is attended with impetuous disengagement of oxygen, which almost completely prevents the oxidizing action of the chlorine. However, this accident may be guarded against by reducing the substance to the very finest powder.

c. Regarding the method of CLOËZ and GUIGNET (by permanganate of potash) see the Analysis of Gunpowder.

B. METHODS BASED ON THE CONVERSION OF THE SULPHUR INTO SULPHURETTED HYDROGEN OR A METALLIC SULPHIDE.

a. The determination of the sulphur in the sulphides of the metals of the alkalies and alkaline earths soluble in water is best effected—

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* Zeitschr. f. anal. Chem. 9, 71.

† *Ib.* 9, 82.

‡ *Ib.* 9, 81.

§ *Ib.* 10, 206.

‖ Compt. Rend. 1835, 865; Journ. f. prakt. Chem. 61, 134.

provided they are free from excess of sulphur—by I., *b* or *c*. In the absence of acids of sulphur you may also convert the sulphur into sulphuric acid by bromine water. The bases are conveniently estimated in a separate portion, which is decomposed by evaporation with hydrochloric or sulphuric acid, or—when none but alkali-metals are present—by ignition with 5 parts of chloride of ammonium in a porcelain crucible. If the compounds contain excess of sulphur they should be oxidized either by chlorine in alkaline solution, or treated according to *B*, *c*, or *C*; if they contain hyposulphite or sulphite, proceed according to § 168.

b. The sulphur contained in alkaline fluids as monosulphide or hydrosulphate of the sulphide may also be determined directly by volumetric analysis, by means of a standard ammoniacal silver or copper solution. In using the former, mix the solution with ammonia, heat and add the standard fluid till on filtering off a small portion, and adding silver solution, a mere opalescence is produced (LESTELLE[*]). In using the copper solution, mix the fluid to be tested with ammonia, heat to 50° or 60°, and add the standard solution, frequently shaking and boiling till no further precipitation of $CuO, 5\,CuS$ is produced, and the solution begins to be blue (VERSTRAET[†]). To make a standard copper solution, 1 c.c. of which shall equal ·01 NaS, dissolve 9·754 pure copper in 40 grm. nitric acid, boil, add 180 to 200 c.c. ammonia and water to 1 litre. These methods are well adapted for technical purposes, for the estimation of sulphide in soda lies for instance. It need hardly be added that precipitated sulphide of silver, copper, or lead (if you have used a solution of oxide of lead in potash) may be estimated gravimetrically.

c. If *all* the sulphur can be expelled from the substance in the form of sulphuretted hydrogen by heating with hydrochloric acid, the sulphide may be heated in a small flask with the concentrated acid to complete decomposition and expulsion of the sulphuretted hydrogen—the latter being determined according to I. If the substance is a fluid, the apparatus on p. 341 (for the expulsion of carbonic acid) is to be recommended for the disengagement of the sulphuretted hydrogen. The tube *h* should be replaced by a small condenser fixed upright (see the Analysis of Black Ash). In the case of polysulphides the sulphur separated in the evolution flask is collected on a filter dried at 100°, washed, dried first at 70°, then for a short time at 100°, and weighed.

C. METHOD BASED ON THE SEPARATION AND WEIGHING OF THE SULPHUR.

The following process has been advantageously employed by M. MORTREUX[‡] for the estimation of sulphur in alkaline polysulphides:—

Extract 10 grm. with boiled water, make the filtrate up by washing to 100 grm. or c.c., and transfer 10 grm. or c.c. (which contain the soluble part of 1 grm. of the substance) to a burette, with a glass tap, of 40 to 45 c.c. capacity, whose exit is cut off obliquely and also narrow. Now add, shaking the closed burette from time to time, a solution of iodine in iodide of potassium (1 part iodine, 5 parts iodide of potassium, 50 parts water) till it just ceases to be decolorized, and a portion of the fluid ceases to brown a piece of paper which has been saturated with solution of sulphate of iron and dried. Add 8—10 c.c. bisulphide of finally on the water-bath, until the fluid smells no longer of chlorine. Proceed now as directed in *a*, *aa*, or *bb*, according as the sulphur is completely dissolved or not. In the latter case you must of course immediately dilute and filter. The oxidation of the sulphur may be usually effected more quickly and completely by warming with nitric acid of 1·36 sp. gr. on a water-bath, and adding chlorate of potash in small portions. Compare STORER,[*] PEARSON, and BOWDITCH.[†]

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* Zeitschr. f. anal. Chem. 2, 94.

† *Ib.* 4, 216.

‡ *Ib.* 1, 390.

THIRD GROUP.

NITRIC ACID.—CHLORIC ACID.

§ 149.

1. Nitric Acid.

I. *Determination.*

Free nitric acid in a solution containing no other acid is determined either by finding its specific gravity or in the volumetric way, by neutralizing with a dilute solution of soda of known strength (comp. Acidimetry). The following method also effects the same purpose: mix the solution with baryta water, until the reaction is just alkaline, evaporate with addition of pure carbonic acid water, nearly to dryness, dilute the residue with water, filter the solution which has ceased to be alkaline, wash the carbonate of baryta, add the washings to the filtrate, and determine in the fluid the baryta as directed in § 101. Calculate for each 1 eq. baryta 1 eq. nitric acid. Lastly, free nitric acid may also be determined in a simple manner by supersaturating with ammonia, evaporating in a weighed platinum dish, drying the residue at 110° to 120°, and weighing the NH_4O,NO_5 (Schaffgotsch). The ammonia should of course be tested to see that it leaves no residue on evaporation.

II. *Separation of nitric acid from the bases, and determination of the acid in nitrates.*

The determination of nitric acid in nitrates is an important and occasionally a difficult problem, which has of late years much occupied the attention of chemists. Before entering upon the consideration of the question, I would lay it down as a general rule, that whatever method may be selected, should always first be tried repeatedly upon weighed quantities of a pure nitrate, that some familiarity with the details of these rather complicated processes may be acquired. Considering the great number of methods that have been proposed, I shall confine myself to describing the simplest and the best.

a. Methods based on the expulsion of the Acid in the Dry Way.

α. In salts of the heavy metals or the earths, the determination of nitric acid may be effected by simple ignition of the anhydrous compound. If we are certain that the oxides remain in the same condition in which they were contained in the decomposed salt, the loss of weight indicates at once the quantity of nitric acid present.

β. In the case of nitrates, whose residue on ignition has no constant composition, or by whose ignition the crucible is much attacked (alkaline and alkaline earthy nitrates), fuse the substance (which must be anhydrous and also free from organic and other volatile bodies) with a non-volatile flux, and estimate the nitric acid from the loss. The following bodies have been proposed as fluxes :—vitrified borax, by v. SCHAFFGOTSCH* (3 parts of borax-glass to 1 part of the nitrate), bichromate of potassa, by PERSOZ† (2 parts to 1 of nitrate), and silicic acid by REICH.‡ All three yield satisfactory results, when the experiments are performed with careful regard to the peculiarities of the individual fluxes.§ Silicic acid is the best, as it may be readily procured, and the execution is the most easy and the most certain to succeed. I shall describe the method in its application to nitrate of potassa or soda.

Fuse the latter at a low temperature, pour out on a warm porcelain dish, powder and dry again before weighing. Now transfer to a platinum crucible 2 to 3 grm. powdered quartz, ignite well and weigh after cooling. Add about ·5 grm. of the salt prepared as above, mix well, and convince yourself by the balance that nothing has been lost during mixing. The covered crucible is then exposed to a low red heat (just visible by day) for half an hour, and weighed after cooling with the cover. The loss of weight represents the quantity of nitric acid. Sulphates or chlorides are not decomposed at the given temperature; if a higher heat be applied, the latter may volatilize. The action of reducing gases must be avoided. The test-analyses, communicated by REICH (*loc. cit.*), as well as those performed in my own laboratory,‖ gave very satisfactory results.

b. Method based on the distillation of the Nitric Acid.

All nitrates may be decomposed by distillation with moderately dilute sulphuric acid. The nitric acid passing into the receiver may then be determined, according to I., volumetrically or gravimetrically. This process, originally recommended by GLADSTONE,¶ was afterwards carefully studied by H. ROSE and FINKENER.** 1 to 2 grm. of the nitrate should be treated with a cooled mixture of 1 volume concentrated sulphuric acid and 2 volumes water. For 1 grm. nitre take 5 c.c. sulphuric acid and 10 c.c. water. The distillation may be performed either with a thermometer at 160° to 170° in a paraffin or sand-bath (duration of the distillation for 1 to 2 grm. nitre, 3 to 4 hours), or *in vacuo*, with the use of a water-bath. The latter process is the best. In the former, the neck of the tubulated retort (which is drawn out and bent down) is connected with a bulbed U-tube containing a measured quantity of normal soda or potassa solution (§ 215.) The distillation *in vacuo* may be conducted, without the use of an air-pump, according to FINKENER, as follows: transfer the measured quantity of water and concentrated sulphuric acid to the tubulated retort, and the necessary quantity of standard potassa or soda solution diluted to 30 c.c. to a flask with a narrow neck of about 200 c.c. capacity. Then, by means of an india-rubber tube, connect the flask with the retort air-tight, so that the drawn-out point of the latter may extend to the body of the flask, and—with tubulure open—heat the contents of the retort and of the flask to boiling. When the air has been expelled from the apparatus by long boiling, transfer the salt (weighed in a small tube) to the retort through the tubulure, close the latter immediately, and at the same time take away the lamp. The retort is then heated with a water-bath, the flask being kept cool. The quantity of nitric acid that has passed over is finally ascertained by determining the still free alkali with standard acid. If it is suspected that all the nitric acid has not been driven into the receiver by one distillation, you may—by heating the flask and cooling the retort—distil the water back into the latter, and then the distillation from the retort may be repeated. The distillate thus obtained is always free from sulphuric acid, hence the results are very exact. The base remains as sulphate in the retort. In the presence of chloride add to the contents of the retort a sufficiency of dissolved sulphate of silver, or—when much chloride is present—moist oxide of silver. The nitric acid is then obtained entirely free from chlorine.

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* Pogg. Annal. 57, 260.

† Répertoire de Chim. appliquée, 1861, 253.

‡ Berg- und Hüttenmannische Zeitschrift, 1861, No. 21; Zeitschr. f. anal. Chem. 1, 86.

§ Zeitschr. f. anal. Chem. 1, 181.

‖ *Ib.* 1, 184.

¶ Chem. Gaz. 1854, 398.

** Zeitschr. f. anal. Chem. 1, 309.

c. Methods based on the decomposition of Nitrates by Alkalies and Alkaline Earths.

a. Nitrates, whose bases are completely separated by caustic or carbonated alkalies—provided basic salts are not precipitated at the same time—may be analysed by simple boiling with an excess of standard potassa or soda or their carbonates. After cooling, dilute to $\frac{1}{4}$ or $\frac{1}{2}$ litre, mix, allow to settle, draw off a portion of the supernatant clear fluid, determine the free alkali remaining in it, and calculate therefrom the amount consumed by the nitric acid. This process was employed by LANGER and WAWNIKIEWICZ,* but was, however, already known. HAYES obtained with the nitrates of silver and bismuth good results; but with the subnitrate of mercury (using carbonate of soda) the results were not so satisfactory.† If the method is applied to nitrate of ammonia you must heat after adding the alkali till all the ammonia is driven off.

It need hardly be mentioned that the method is inapplicable in the presence of any other acid.

β. In nitrates whose bases are precipitated by baryta, lime or their carbonates (or by freshly prepared hydrosulphate of sulphide of barium free from hyposulphite, CLAUS‡) the acid may be estimated by precipitating hot or cold, filtering, passing carbonic acid if necessary, heating, filtering, and estimating the baryta by sulphuric acid. 1 eq. = 1 eq. nitric acid. In applying the method to nitrate of bismuth you must boil after adding the hydrate of baryta till the oxide of bismuth is yellow (RUGE, LUDDECKE§).

d. Methods based upon the decomposition of the Nitric Acid by Protochloride of Iron.

a. PELOUZE‖ was the first to turn the action of free nitric acid upon protochloride of iron to account for the determination of nitric acid. The decomposition is as follows:

$$6FeCl + KO,NO_5 + 4HCl = 4HO + KCl + 3Fe_2Cl_3 + NO_2.$$

In PELOUZE's method a known quantity of protochloride of iron in excess is used, and the portion which remains unchanged determined by permanganate. His method of operating is given in the note;* it gives occasionally satisfactory results, but can never be relied on, in which view all agree who have subjected the question to a critical examination (compare **Fr. Mohr**,† and **Abel** and **Bloxam**‡). The results of numerous experiments made in my own laboratory lead to the same conclusion.

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* Annal. d. Chem. u. Pharm. 117, 230.

† H. ROSE, Zeitschr. f. anal. Chem. 1, 306.

‡ Zeitschr. f. anal. Chem. 1, 372.

§ *Ib.* 6, 233.

‖ Journ. f. prakt. Chem. 40, 324.

The following may be mentioned as causes of the defectiveness of the method:—

a. Action of the air upon the nitric oxide present in the flask with aqueous vapor, which leads to the re-formation of nitric acid; this may be held to be the principal cause of the inaccuracy of the method.

b. Incomplete expulsion of the nitric oxide from the fluid, which leads to the reduction of a larger amount of permanganate than corresponds to the protochloride of iron; this is to be apprehended only in the case of dilute solutions.

c. Escape of nitric acid before it has acted upon the protochloride of iron; this is to be apprehended in cases where the fluid, after addition of the nitrate, is boiled very rapidly, and the excess of protochloride of iron is comparatively small.

d. Occasionally also loss of iron, owing to want of proper care in boiling, and to be apprehended more especially if part of the protochloride of iron deposits on the sides of the vessel above the fluid, in the solid state.

I have succeeded in modifying **Pelouze**'s process so as to avoid all these sources of error, and to obtain perfectly accurate and reliable results. My process is conducted as follows:—

Select a tubulated retort of about 200 c.c. capacity, with a long neck, and fix it so that the latter is inclined a little upwards. Introduce into the body of the retort about 1·5 grm. fine pianoforte wire, accurately weighed, and add about 30 or 40 c.c. pure fuming hydrochloric acid. Conduct now through the tubulure, by means of a glass tube reaching only about 2 cm. into the retort, hydrogen gas washed by solution of potassa, or (preferably) pure carbonic acid, and connect the neck of the retort with a U-tube containing some water. Place the body of the retort on a water-bath, and heat gently until the iron is dissolved. Let the contents of the retort cool in the current of hydrogen or carbonic acid; increase the latter, and drop in, through the neck of the retort, into the body, a small tube containing a weighed portion of the nitrate under examination, which should not contain more than about ·2 grm. of nitric acid. After restoring the connexion between the neck and the U-tube, heat the contents of the retort in the water-bath for about a quarter of an hour, then remove the water-bath, heat with the lamp to boiling, until the fluid, to which the nitric oxide had imparted a dark tint, shows the color of sesquichloride of iron, and continue boiling for some minutes longer. Care must be taken to give the fluid an occasional shake, to prevent the deposition of dry salt on the sides of the retort. Before you discontinue boiling, increase the current of hydrogen or carbonic acid, that no air may enter through the U-tube when the lamp is removed. Let the contents cool in the current of gas, dilute copiously with water, and determine the iron still present as protochloride with bichromate or permanganate. 168 of iron converted by the nitric acid from the state of proto- to that of sesquichloride correspond to 54·04 of nitric acid. My test-analyses of pure nitrate of potassa gave 100·1—100·03—100·03 and 100·05, instead of 100.*

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* Dissolve 2 grm. pianoforte wire in 80—100 c.c. pure concentrated hydrochloric acid, with the aid of heat, in a flask holding about 150 c.c., which is closed by a cork with a glass tube fitted in it. When the wire is dissolved, add 1·2 grm. of the nitrate of potassa or an equivalent quantity of another nitrate to be analysed, replace the cork, and heat rapidly to boiling. After 5 or 6 minutes, pour the fluid, which has now again cleared, into a larger-sized flask, dilute largely with water, and titrate with permanganate.

† Lehrbuch der Titrirmethode, 1, 216.

‡ Quart. Journ. Chem. Soc. 9, 97.

β. Since we have learnt how to titrate sesquioxide of iron with accuracy directly, it is, as a rule, more convenient and exact, not (as in *a*) to estimate the protoxide of iron remaining unoxidized after the action of the nitric acid, but, as C. D. **Braun**† has pointed out, to determine the sesquioxide produced. I can recommend the following mode of operating as the best.‡ Besides the requisites for titrating sesquioxide of iron by means of protochloride of tin, given p. 225, you must have an acid solution of protoxide of iron, which is conveniently prepared by dissolving 100 grm. sulphate of iron (as free as possible from sesquioxide) in 150–200 c.c. hydrochloric acid of 1·10–1·12 sp. gr. by the aid of heat in a ½ litre flask, and filling up to the mark with strong hydrochloric acid. As, however, it is not easy to keep this solution perfectly free from sesquioxide, the small quantity of the latter present is determined with protochloride of tin in 50 c.c. (p. 225). It is well to heat the solution in a current of carbonic acid and titrate it immediately before or after the analysis.

Transfer the weighed nitrate (containing not above ·2 nitric acid) to a long-necked flask, fitted with a doubly perforated cork. The latter carries two glass tubes, one of which nearly reaches into the body of the flask, while the other only just enters it. Pass carbonic acid through the former till all the air is driven out, add 50 c.c. of the sulphate of iron solution, pass the gas again for some time, then heat, at first gently, gradually to boiling, till the fluid has lost its blackish color, and has taken the pure tint of the sesquichloride of iron, and till the escaping gas ceases to blue dilute starch-paste mixed with iodide of potassium when passed into it. Now remove the cork with the tubes, rinse the longer one if necessary, and after diluting with twice its volume of water, determine the sesquichloride present according to p. 225. The cooling (for the purpose of estimating the small excess of tin solution with iodine) is advantageously conducted in the stream of carbonic acid. Deduct from the protochloride of tin used first the small excess, ascertained by iodine solution, secondly the slight amount, corresponding to the sesquioxide contained in the 50 c.c. of protoxide of iron solution employed; the remainder gives the iron in the sesquioxide produced, and, if this is multiplied by ·32167, the nitric acid. This factor is obtained thus :—

$$6\text{eq.Fe}(168) : 1\text{eq.NO}_5(54{\cdot}04) :: \text{the iron present as sesquioxide} : x.$$

It will be seen that it is best, once for all, to multiply the known quantity of iron in 10 c.c. of the solution of sesquichloride used to standardize the tin solution, by the above factor, and to mark the product on the bottle as the corresponding quantity of nitric acid. If you have no standard sesquichloride of iron, you may standardize the tin directly on nitric acid, by adding a weighed quantity of nitrate of potash to 50 c.c. of the sulphate of iron solution, and determining the sesquichloride of iron produced as above. Results thoroughly good when the work is correct, and all the estimations succeed each other immediately.*

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* Annal. d. Chem. u. Pharm. 106, 217.

† Journ. f. prakt. Chem. 81, 421.

‡ Where one or two estimations only are to be made you may dissolve iron wire in hydrochloric acid as in *a*.

γ. Schlösing's method.†

The following method, employed by Schlösing, more particularly to determine nitric acid in tobacco, and which affords this very important advantage, that it may be used in presence of organic matter, has successfully passed through the ordeal of numerous and searching experiments.

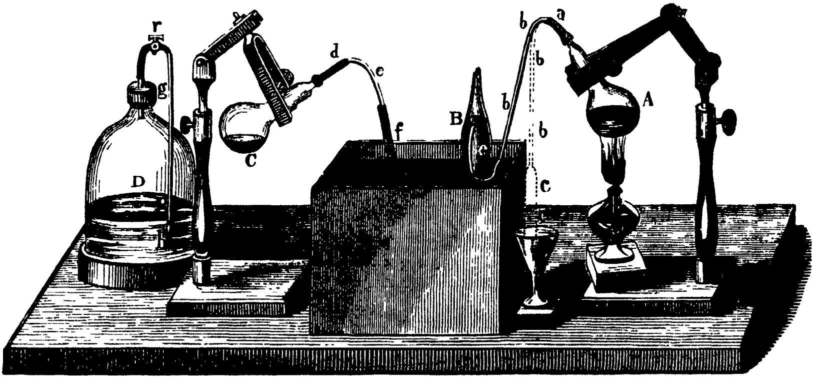

Fig. 99.

The process is conducted in the apparatus shown in fig. 99.

The dissolved nitrate is introduced into the balloon *A*, whose drawn-out neck is connected, by means of an india-rubber tube *a*, with a narrow glass tube *b*; *c* is another caoutchouc-tube connected with *b*, and 15 cm. long. The solution of the salt, which must be neutral or alkaline, is boiled down to a small volume, the aqueous vapor completely expelling the air from *A* and the tubes; *c* is dipped into a glass containing a solution of protochloride of iron in hydrochloric acid; the lamp removed, and the receding regulated by compressing the caoutchouc-tube *c* with the fingers; when the iron solution is nearly absorbed, some hydrochloric acid is allowed to recede, three or four times, in separate portions, to free the tube completely from protochloride of iron, which is absolutely necessary. Before air can force its way, *c* is closed by an iron clip, dipped under the mercury in the trough, and the end placed under the bell *B*. The lamp is now replaced under *A*, to allow the reaction to proceed; immediately after, the clip is replaced by the compression of the fingers, which are also removed from it as soon as a pressure is felt from within. The reaction is generally terminated in about eight minutes, when *c* is removed from under *B*. The latter is a small bell-jar, made out of an adapter; it must hold three or four times the volume of the gas to be received; in cases where the evolution of gas is rather impetuous, it is occasionally necessary to submerge the bell-jar in the trough, to effect a more speedy cooling of the vapor. The upper part of *B* is drawn out, as shown in fig. 100, to facilitate its subsequent insertion into the caoutchouc-tube, and also the breaking off of the point. The bell-jar is first filled with water, to expel the air from it, then with mercury; milk of lime, previously boiled, is then finally introduced into it, by means of a curved pipette, which serves to free the nitric oxide entering *B* from every trace of acid vapor. The nitric oxide has now to be transferred to the balloon *C*, to be there reconverted into nitric acid by oxygen. The balloon *C* contains some water; it is connected by a caoutchouc-tube, *d*, with a glass-tube, *e*, which bears at the opposite end another thin caoutchouc-tube *f*, 10 cm. in length.

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* Zeitschr. f. anal. Chem. 1, 38. Holland gives a method in which the use of hydrogen or carbonic acid is dispensed with, Chem. News, 17, 219.

† Annal. de Chim. (3) 40, 479.

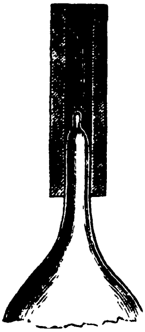

Fig. 100.

The water in *C* is now heated to boiling, until *all* air is expelled from the balloon and the tubes by the aqueous vapor; *f* is connected with the point of the bell-jar *B*, which has just before been slightly scratched with a diamond, and the end of the point is then broken off. The aqueous vapor condenses at first in the bell-jar, and at the same time expels the small quantity of milk of lime remaining in the point. But if the lamp is now removed, a current in the opposite direction speedily sets in, which drives the nitric oxide into the balloon *C*. Should this proceed too rapidly, *f* need simply be compressed with the fingers. As soon as the milk of lime in the bell-jar has nearly reached the rim of *f*, *f* is closed by a clip. To transfer the last traces of the nitric oxide to *C*, pure hydrogen (20 or 30 c.c.) is conducted into the bell-jar, and allowed to be absorbed as before. *f* is then closed by the clip, its end taken off from the point of the bell-jar, and connected instead with the glass-tube *h*, of the oxygen-jar *D*; the cock *r* is now opened, and then the clip also, which will cause oxygen to pass into *C*. When the object of the operation has been attained, *r* is closed, and *h* and *f* are disconnected; after waiting a quarter of an hour, the nitric acid reproduced is determined by means of very dilute solution of soda (§ 215).

The success of this method depends essentially upon the complete expulsion of the air from *A* and *C*. SCHLÖSING obtained highly satisfactory results by it. Some test-analyses made in my own laboratory,* and by R. FRÜHLING,† and H. GROUVEN, and E. SCHULZE,‡ were also unimpeachable. Where the quantity of nitric acid is only small, it is advisable to increase the amount of protochloride of iron considerably.

It will be evident at once that while retaining the principle of this method, the apparatus may be modified in various ways. SCHLÖSING recommends for the estimation of quantities of nitric acid under ·01 grm. a slightly different apparatus. FRÜHLING and GROUVEN made several changes in the apparatus, but these were not of great importance. E. REICHARDT* dispenses with the mercurial trough, and receives the nitric oxide in a vessel filled with soda solution, after having expelled all the air by means of hydrogen. As, however, it is difficult to procure hydrogen free from oxygen, this modification is liable to give low results.

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* Zeitschr. f. anal. Chem. 1, 39.

† Landwirthschaftl. Versuchsstat 9, 14, and 150.

‡ Zeitschr. f. anal. Chem. 6, 384.

In SCHULZE's modification, described by H. WULFERT,† the evolved nitric oxide is received in a bell-glass provided with a glass tap and filled with mercury, then passed into a measuring tube and measured. In the presence of a foreign gas, the latter is determined by absorbing the nitric oxide with protochloride of iron. WULFERT, however, never found more than ·33 c.c. of gas left unabsorbed. The results were excellent, even with very minute quantities of nitric acid, and in the presence of much organic matter.

c. Methods based on the conversion of the Nitric Acid into Ammonia.

If a nitrate is heated in an alkaline fluid in which hydrogen is evolved in the nascent state in sufficient quantity, all the nitric acid may be converted into ammonia,‡ so that from the amount of the same the quantity of the nitric acid may be accurately deduced. SCHULZE§ was the first to apply this principle to the estimation of nitric acid, W. WOLF,|| HARCOURT,¶ and SIEWERT** soon followed. Subsequently the method and the apparatus were modified by BUNSEN†† and HAGER.‡‡ SCHULZE reduces with platinized zinc; W. WOLF, HARCOURT, and SIEWERT with zinc and iron-filings; BUNSEN with a zinc-iron spiral. The employment of zinc and iron appears to give the best results; I shall, therefore, first describe HARCOURT's process, in which aqueous solution of potash is used, and then SIEWERT's, in which alcoholic solution of potash is used. Organic matter destroys the accuracy of the results (FRÜHLING§§). Opinions differ considerably regarding the value of the method, even in the absence of organic matter. Although HARCOURT's and SIEWERT's test-analyses were unexceptionable, WOLF (*loc. cit.*) gives the following three conditions as essential to success: (1) The conversion of the nitric acid into ammonia must take place in the cold—by heating during the evolution of hydrogen, ammonia is lost, probably from the escape of nitrogen as such; (2) To obtain a good and uniform evolution of hydrogen, zinc and iron must be used in conjunction; (3) The potash or soda must be dissolved in from 7 to 8 parts of water, neither more nor less. These directions are, in part, quite inconsistent with those given by HARCOURT. FINKENER|||| rejects all methods founded on this principle, on the grounds that, although the whole of the nitric acid is decomposed, it is not all converted into ammonia. For myself, I have not studied the method enough to pronounce authoritatively upon it; but I must say, that both HARCOURT's and SIEWERT's processes have generally given me good results.

HARCOURT employs the apparatus represented in fig. 101. Begin

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* Zeitschr. f. anal. Chem. 9, 24. † *Ib.* 9. 400.

‡ The conversion in acid solution is only partial.—L. GMELIN, MARTIN.

§ Chem. Centralbl 1861, 657 and 833.

|| Chem. Centralbl. 1862, 379; Journ. f. prakt. Chem. 89, 93; Zeitschr. f. anal. Chem. 2, 401.

¶ Journ. Chem. Soc. 15, 385. ** Annal. d. Chem. u. Pharm. 125, 293.

†† Zeitschr. f. anal. Chem. 10, 414. ‡‡ *Ib.* 10, 334.

§§ Landwirthschaftl. Versuchsstat. 8, 473.

|||| H. ROSE, Handb. d. anal. Chem. 6 Aufl. von FINKENER, ii. 829.

by bringing the tube *e* into the vertical position, by turning it half-round in the tubulure, then run in from the burette an excess of standard acid, it will occupy *d*, add some tincture of litmus, turn the tube *e* back again as represented, and run a little more acid into the bulbs. Now remove the flask *a*, while the tube and cork, as well as the little flask *b* containing some water, remain in unchanged position on the sand-bath, and transfer to *a* about 50 grm. finely granulated zinc, and 25 grm. iron-filings which have been purified by sifting and subsequent ignition in a current of hydrogen, then add the weighed nitrate (*e.g.*, ·5 nitre), 20 c.c. water and 20 c.c. potassa solution of 1·3 sp. gr. Now heat the part of the sand-bath *c*, which is under *a*, till the contents of *a* boil. If the bubbles of air and hydrogen pass quietly in *e*, loss of ammonia is not to be feared. As soon as the distillation has commenced, place the lamp so that the water in *b* also gently boils. The fluid is thus twice distilled in one operation, and the traces of potassa, which pass out of *a*, are completely retained in *b*. The end of each exit-tube is—as a further precaution—drawn out and bent up in the form of a hook. The distillation requires 1 to 2 hours. It may be broken off, when the hydrogen (which is disengaged in larger quantity as the potassa solution becomes more concentrated), has passed through the bulb-tube *e* 5 or 10 minutes regularly. As soon as the fluid in *e* has receded to *d*, in consequence of the cooling of the apparatus, remove the caoutchouc stopper from the small tubulure *f*, and rinse the condenser with a stream of water, so as to be sure of getting the last traces of ammonia into the receiver. Now turn round the tube *e* to bring it into a vertical position, rinse it out with water, take it away and close the tubulure of the receiver with a cork. Finally, remove the receiver, rinse the outside of the condenser at the end, and proceed to titrate the free acid remaining. The metals remaining in *a* only want to be washed with water, dilute acid and water again, and they can be used for a second determination. It is true that when they have been once used they evolve hydrogen far slower than bright zinc and freshly-ignited iron, but the disengagement of ammonia proceeds equally well in both cases. Chlorides and sulphates have no influence on the operation. In the presence of oxide of lead it appears desirable to add sulphate of potassa.

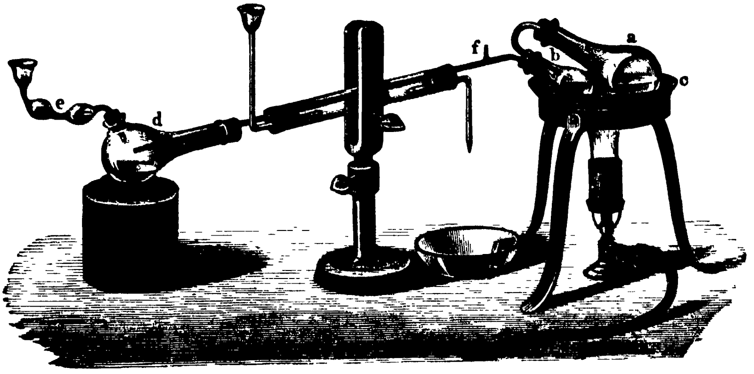

Fig. 101.

Siewert employed to about 1 grm. nitre 4 grm. iron-filings and 8 to 10 grm. zinc-filings, and also 16 grm. solid hydrate of potassa and 100 c.c. alcohol, of ·825 sp. gr. By the use of alcohol the danger of the boiling fluid receding is got rid of. His apparatus consists of a flask of 300 to 350 c.c. capacity with evolution tube, which leads to the flasks represented in fig. 102. The capacity of each is 150 to 200 c.c.; they contain standard acid. The connecting tube *b* is ground obliquely at both ends, *c* serves during the operation to hold a strip of litmus paper and after it to enable the analyst to transfer the fluid from one flask to the other at will. After the apparatus has been put together, the disengagement of gas may be allowed to go on in the cold, or it may be assisted from the first by a small flame. After the lapse of half-an-hour the ammonia formed begins to pass over in proportion as the alcohol distils off. As soon as the latter is fully removed from the evolution flask, heat is applied with great caution—to drive out the last traces of ammonia—till steam appears in the evolution tube, or 10 to 15 c.c. alcohol are rapidly introduced once or twice into the evolution flask and distilled off.

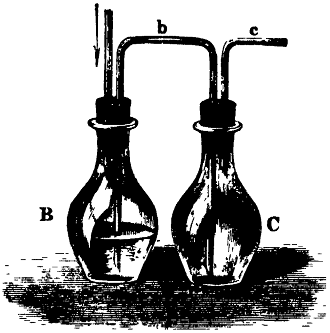

Fig. 102.

f. Method depending on the estimation of the loss of Hydrogen, after **Fr. Schulze**.*

If aluminium be dissolved in solution of potassa, aluminate of the alkali is formed with evolution of hydrogen; the amount of hydrogen evolved corresponds to the quantity of aluminium dissolved; and if a nitrate be added to the mixture evolving hydrogen, less gas is disengaged than would otherwise be the case, for a part of the nascent hydrogen serves to convert the nitric acid into ammonia ($NO_5 + 8H = NH_3 + 5HO$); this deficit of hydrogen is, of course, proportional to the amount of nitric acid converted into ammonia. According to **Schulze** the decomposition is complete, if the process is carried on slowly (**Finkener**† contradicts this). A minute quantity of nitric acid gives rise to a relatively large deficit of hydrogen, hence this method can be applied to the estimation of small amounts of acid. E. **Schulze**‡ states that the method cannot be used in the presence of organic matter. In such a case you must subject the substance to the following preliminary treatment:—Heat with solution of potash till all ammonia is expelled, add a concentrated solution of pure permanganate of potash, boil for 10 minutes (after which the fluid should remain red), add some formic acid to decompose the permanganic acid present, filter, wash, concentrate, neutralize exactly with sulphuric acid, and finally evaporate to a small bulk if necessary (Fr. **Schulze**§).

I shall describe the apparatus which is somewhat similar to

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* Zeitschr. f anal. Chem. 2, 300.

† H. **Rose**, Handb. d. anal. Chem. 6 Aufl. von **Finkener**, ii. 829.

‡ Zeitschr. f. anal. Chem. 6, 379.

§ Zeitschr. f. Chem. (N. F.) 4, 296.

Knop's azotometer,* and afterwards proceed to the execution of the analysis.

The flask *A* (fig. 103) holds about 50 c.c., into its neck the tube *B*, which is expanded above into a bulb, is ground air-tight; the glass rod

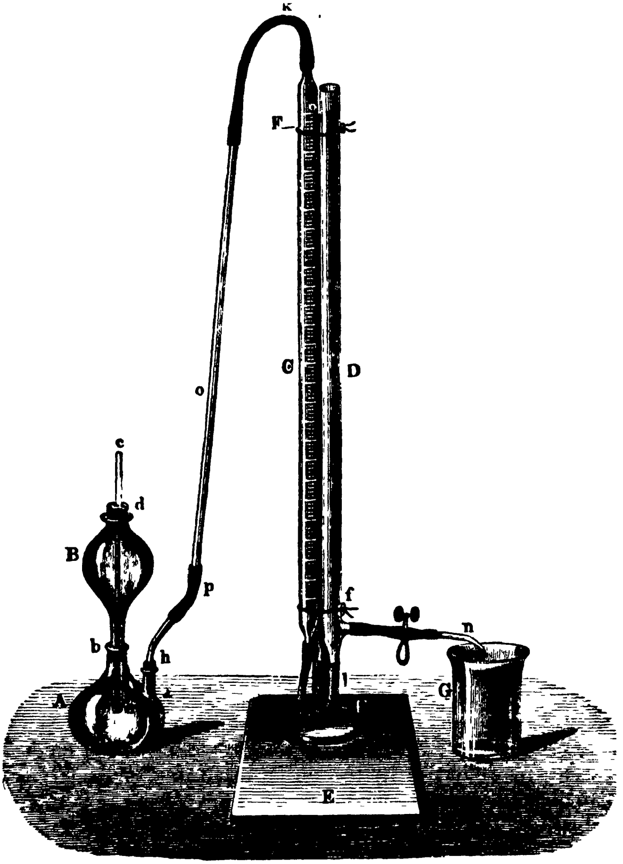

Fig. 103.

c is ground into the lower opening of *B*, and closes it completely; this rod passes through the cork *d*, and is long enough to enable the operator to introduce fluid into *B* by means of a pipette, when the cork is raised to the top. The tube *C*, divided into $\frac{1}{10}$ c.c., serves to measure the gas; it is connected by means of the flexible tube *l*, with the plain tube *D*, which is of similar width. The tubulure *f* is provided with spout and stop-cock, as shown in the drawing. The upper opening of *C* is connected by the india-rubber tube *k* with a tube of small calibre, and the latter again with the tube *h*, which is fitted with a cork into the tubulure *a*.

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* Chem. Centralbl. 1860, 244. The original Knop's apparatus differs from the modification figured in the text only in this, that the tube *D* is not provided with the lateral tubulure below. The removal of water from *D* is effected by sucking it into a flask. Rautenberg's modification consists in placing the tubes *C* and *D* in a cylinder filled with water, which enables the operator to regulate and determine the temperature of the gas on measuring, more conveniently. Instead of the apparatus given in the text, you may use that of Rumpf—Zeitschr. f. anal. Chem. 6, 399.

To perform a series of experiments, a rather large quantity of aluminium filings will be required. Any particles of steel should be removed from the same by a magnet. The first thing is to determine the *weight* of hydrogen yielded by a weighed quantity of this aluminium powder on its solution in potash. This preliminary experiment is absolutely indispensable, as each kind of aluminium behaves differently in this respect. Introduce into *A* an exactly weighed quantity of aluminium powder, about ·075 grm., and add some water. Introduce into *B* exactly 5 c.c. potash solution, and join *A* and *B* as represented. Now pour water into *D* till it stands exactly at the upper mark in *C*—*i.e.*, the zero—and connect *A* with the measuring apparatus by inserting the tube *h* into the caoutchouc tube *p*. Having again satisfied yourself that the water in *C* and *D* is at the same height, and in *C* stands at zero, note the temperature of the room and place *A* in a beaker with water of the same degree. Now allow water to run out at *n* till the surface of the fluid in *D* stands exactly at a certain mark, say at 30 c.c., and in *C* has sunk to about the mark 1. If after some time both levels have remained unchanged, and you are therefore convinced that the apparatus is air-tight, raise the glass-rod *c* slightly, allowing the potash in *B* to flow into *A*. As on account of the lower level in *D*, the air in *A* is under less pressure than the air in *B* or the free atmosphere, care must be taken that the opening at *c* is closed, the moment that the fluid in *B* has almost run out and just enough remains to prevent free communication between *A* and *B*. The volume of the fluid originally introduced into *B* (according to the above, 5 c.c.) is subsequently to be deducted from that of the gas in *C*. In proportion as the aluminium dissolves, and hydrogen is evolved, the level in *C* sinks, while the column of water in *D* rises and renders it necessary to draw off water at *n*, in order that both levels may remain about the same. When the evolution of gas in *A* has ceased, and you have satisfied yourself that the temperature of the water in which *A* stands, and also of the air, is the same as at the beginning, bring the water in *D* to the same level as that in *C*, so that the tension of the gas in *A* and *C* may correspond exactly to the atmospheric pressure, as before the beginning of the experiment, and then read off the height of the fluid in *C*. The number so observed, *minus* the c.c. of fluid which flowed from *B* into *A*, expresses the c.c. hydrogen evolved by the solution of the aluminium, under the existing circumstances of atmospheric pressure, temperature, and tension of aqueous vapor. Reduce the measured volume to the dry condition, 0° and 760 mm. (§ 198), calculate the weight of this volume of hydrogen (1000 c.c. = ·08961 grm.), and divide the aluminium used by the number found, the quotient gives us the number of grammes of aluminium which evolve 1 grm. hydrogen. SCHULZE found this quotient in one case to be 10·5042 (9·16 of pure aluminium would yield 1 grm. hydrogen). Now 8 eq. hydrogen (8) correspond to 1 eq. nitric acid (54·04), hence 8 × 10·5042 = 84·0336 grm. of the aluminium in question correspond to 54·04 grm. nitric acid.

We will now suppose that the exact value of the aluminium for our purpose being known, we are about, on some other occasion, to make a nitric acid determination with its aid. Begin by calculating how many c.c. hydrogen is yielded by a definite weight of aluminium, say ·050 grm. for this particular day, *i.e.*, the existing temperature and pressure. I may remark in passing that it is taken for granted that these remain constant throughout the process; a room should be chosen which is not liable to variations of temperature. Let us suppose, under the circumstances obtaining, 58·4 c.c. hydrogen correspond to ·050 grm. aluminium. Introduce the fluid to be analysed—say about 20 c.c.—into the flask *A*, add a weighed quantity of aluminium powder (at least 2 parts to 1 of nitric acid), arrange the apparatus as above directed, and allow the potassa at first to flow only drop by drop into *A*. The solution of the aluminium must be so conducted that a scarcely visible evolution of hydrogen may be kept up for at least an hour, and the whole process should take 3 or 4 hours. Convince yourself that the pressure and temperature are the same as at the beginning, and read off.

Let us take one of SCHULZE'S experiments as an illustration. ·15 grm. of the aluminium powder of the value above given, and a known quantity of nitrate of potash were employed, 95·6 c.c. hydrogen were obtained. How much nitric acid was present? ·15 grm. aluminium would have evolved 3 × 58·4 = 175·2 c.c. hydrogen, but we have only obtained 95·6 c.c.: therefore the deficit is 79·6 c.c., which, according to the proportion

$$58·4 : 79·6 :: ·050 : x \qquad x = ·06815$$

corresponds to ·06815 aluminium, which, according to the proportion

$$84·0336 : 54·04 :: ·06815 : x \qquad x = ·04383$$

corresponds to ·04383 nitric acid.

The amount of nitrate of potash actually employed was ·083 grm., which contains theoretically ·0443 NO_5.

g. Methods in which the Nitrogen is separated in the gaseous form, and measured or weighed.

These methods are especially applicable to nitrates, which, when ignited, are decomposed into oxide or metal and compounds of nitrogen; they will be found in § 185, under the head *Analysis of Organic Bodies*. MARIGNAC analysed the compounds of nitric acid and suboxide of mercury in this manner. BROMEIS analysed the nitrites, &c., of lead by a method given by BUNSEN.* These methods can hardly be dispensed with where the water of nitrates has to be estimated directly.

If you wish to estimate the nitrogen gravimetrically, which is obtained by igniting a nitrate with finely divided copper, you may employ GIBBS'S method.†

h. The methods which are employed for the estimation of nitric acid in natural waters will be found under the head of *Water Analysis*.

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* Annal. d. Chem. u. Pharm. 72, 40.

† Zeitschr. f. anal. Chem. 3, 393.

§ 150.

2. Chloric Acid.

I. *Determination.*

In the absence of other compounds of chlorine, free chloric acid in aqueous solution may be determined by converting it into hydrochloric acid (II., *c* and *d*), and determining the acid formed, as directed § 141; or by saturating with solution of soda, evaporating and treating the residue as directed in II., *a* or *b*.

II. *Separation of Chloric Acid from the Bases and Determination of the Acid in Chlorates.*

a. After Bunsen.* When warm hydrochloric acid acts upon chlorates, the latter are reduced; as this reduction is not atended with separation of oxygen, the following decompositions may take place:—

$$\begin{matrix}\mathrm{ClO_5}\\\mathrm{HCl}\end{matrix}\left\{\begin{matrix}\mathrm{ClO}\\\mathrm{ClO_3}\\\mathrm{HO}\end{matrix}\right.\quad\begin{matrix}\mathrm{ClO_5}\\\mathrm{2HCl}\end{matrix}\left\{\begin{matrix}\mathrm{3ClO}\\\mathrm{2HO}\end{matrix}\right.\quad\begin{matrix}\mathrm{ClO_5}\\\mathrm{3HCl}\end{matrix}\left\{\begin{matrix}\mathrm{2ClO}\\\mathrm{2Cl}\\\mathrm{3HO}\end{matrix}\right.\quad\begin{matrix}\mathrm{ClO_5}\\\mathrm{4HCl}\end{matrix}\left\{\begin{matrix}\mathrm{ClO}\\\mathrm{4Cl}\\\mathrm{4HO}\end{matrix}\right.\quad\begin{matrix}\mathrm{ClO_5}\\\mathrm{5HCl}\end{matrix}\left\{\begin{matrix}\mathrm{6Cl}\\\mathrm{5HO}\end{matrix}\right.$$

Which of these products of decomposition may actually be formed, whether all or only certain of them cannot be foreseen. But no matter which of them may be formed, they all of them agree in this, that, in contact with solution of iodide of potassium, they liberate for every 1 eq. chloric acid in the chlorate, 6 eq. iodine. 761·1 of iodine liberated correspond accordingly to 75·46 of chloric acid. The analytical process is conducted as described § 142, 1. The test analysis adduced by Bunsen is favorable. According to Finkener,† however, this method gives too little iodine, and he therefore recommends boiling a mixture of 33 c.c. hydrochloric acid, 66 c.c. water, 10 grm. iodide of potassium, and 1 c.c. aqueous sulphurous acid for five minutes in a current of carbonic acid, allowing to cool in the gaseous current, and then adding this solution to the chlorate in a stoppered bottle. The bottle should be previously filled with carbonic acid and then filled up with the solution. It is closed firmly and heated for fifteen minutes in a water-bath, allowed to cool thoroughly and shaken; the fluid is finally diluted, and the free iodine estimated.

b. The weighed chlorate is heated in an excess of solution of sulphate of iron in hydrochloric acid, and the sesquichloride of iron produced is estimated. The process is conducted as directed § 149, II., *d*, *β*. 12 eq. iron converted from the condition of protochloride into that of sesquichloride correspond to 1 eq. chloric acid.

c. The conversion of chloric acid (and generally of all oxygen compounds of chlorine, except perchloric acid) may be also effected in dilute aqueous solution by nitrous acid or a nitrite, preferably by neutral nitrite of lead (Toussaint‡). The dilute aqueous solution of the chlorate is mixed with a slight excess of solution of nitrite of lead,§

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* Annal. d Chem. u. Pharm. 86, 282.

† H. Rose, Handb. der analyt. Chemie, 6 Aufl. von Finkener, ii. 612.

‡ Annal d. Chem u. Pharm. 137, 114.

§ Take 1 part of nitrate of lead, 1½ parts of lead and 50 parts of water, and boil them together for a long time. The solution first turns yellow and finally loses all color. Cool the solution rapidly when quadribasic nitrite of lead ($4PbO,NO_3,HO$)

acidified with nitric acid, and warmed. The hydrochloric acid produced is converted into chloride of silver (§ 141, I., *a*).

If you wish to apply this principle to the volumetric estimation of chloric acid proceed as follows:—Mix a very dilute standard solution of chlorate of potash in a stoppered bottle with excess of nitrate of silver, acidify strongly with nitric acid, heat in a water-bath, and add the nitrite of lead till a fresh drop no longer produces a precipitate of chloride of silver. The liquid should be frequently shaken to favor the separation of the chloride of silver. The solution of nitrite of lead being thus standardized may be used for the estimation of unknown quantities of chloric acid. The author's test analyses gave good results, which were corroborated by experiments in this laboratory.

d. The reduction of chloric acid may be also effected by means of hydrated protoxide of iron. Mix the solution of the alkaline chlorate with a sufficiency of pure sulphate of iron, supersaturate strongly with potash free from chlorine, boil for some time, filter off the protosesquioxide of iron thrown down, wash, acidify the filtrate with nitric acid, and precipitate the chlorine with solution of silver (§ 141, I., *a*—C. STELLING*). From my own experiments I find that it is well to make the filtrate up to 250 c.c., and test a portion for chloric acid by acidifying with sulphuric acid, adding a minute quantity of indigo solution, and then a little sulphurous acid. Having satisfied yourself that all the chloric acid has been reduced, you may then estimate the chlorine as silver salt in an aliquot part of the 250 c.c.

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will fall down as a white powder. Suspend this powder in water and pass carbonic acid till the basic salt is entirely decomposed. Filter and preserve the solution in filled bottles.

* Zeitschr. f. anal. Chem. 6, 32.

SECTION V.

SEPARATION OF BODIES.

§ 151.

In the previous Section we have considered the methods employed for the determination of bases and acids, when only one base or one acid is present. In the present Section we shall treat of the separation of bodies, *i.e.*, the determination of the bases and acids, when several bases or acids are present.

The separation of bodies may be effected in three ways, viz., *a*, by *direct analysis*: *b*, by *indirect analysis*; *c*, by *estimation by difference.*

By *direct analysis*, we understand the actual separation of the bases or acids. Thus, we separate potash from soda by bichloride of platinum; copper from tin by nitric acid; arsenic from iron by sulphuretted hydrogen; iodine from chlorine by nitrate of protoxide of palladium; nitric acid from sulphuric acid by baryta; carbon from nitrate of potassa by water, &c. &c. In direct analysis we render one body insoluble, while the others remain in solution, or *vice versâ*, or we volatilize one body, leaving the others behind, or we effect actual separation in some other manner. This is the mode of analysis most frequently employed. It generally deserves the preference where choice is permitted.

We term an analysis *indirect*, if it does not effect the actual separation of the bodies, but causes certain changes which enable us to calculate the quantities of the bases or acids present. Thus the quantity of potash and soda in a mixture of the two may be determined by converting them into chlorides, weighing the latter, and estimating the chlorine (§ 152, 3).

Finally, if we weigh two bodies together, determine one of them, and subtract its weight from that of the two, we shall find the weight of the other body. In this case the second body is said to be *estimated by difference.* Thus, alumina may be determined when mixed with sesquioxide of iron, by weighing the mixture and estimating the iron volumetrically.

Indirect analysis and estimation by difference may be employed in an exceedingly large number of cases; but their use is as a rule only to be recommended where good methods of true separation are wanting. The special cases in which they are preferable to direct analysis cannot be all foreseen; those alone are pointed out which are of more frequent occurrence. As regards the calculations required in indirect analysis, I have given general directions under "the Calculation of Analysis;" wherever it appeared judicious, I have added the necessary directions to the description of the method itself.

I have retained our former subdivision into groups, and, as far as practicable, systematically arranged, first, the general separation of all the bodies belonging to one group from those of the preceding groups; secondly, the separation of the individual bodies of one group from all or from certain bodies of the preceding groups; and finally, the separation of bodies belonging to one and the same group from each other. I think I need scarcely observe that the general methods which serve to separate the whole of the bodies of one group from those of another group, are also applicable to the separation of every individual body of the one group from one or several bodies of the other group. It must not be understood that the more special methods are necessarily in all cases preferable to the more general ones. As a rule it must be left to individual chemists to decide for themselves in each special case which method should be adopted. With respect to the general methods for separating one group from another, I would observe that those adduced appeared to me more adapted to the purpose than others, but still there may be others that are equally suitable, and in special cases even more so. A wide field is here open to the ingenuity of the analyst.

The methods given for the separation of both bases and acids are generally based upon the supposition that they are in the free state, or in the form of salts soluble in water. Wherever this is not the case, special mention is made of the circumstance.

From among the host of proposed methods, I have, as far as practicable, chosen those which have been sanctioned by experience and are distinguished for accurate results. In cases where two methods were on a par with each other as regards these two points, I have either given both, or selected the more simple one. Methods which experience has shown to be defective or fallacious have been altogether omitted. I have endeavoured to point out, as far as possible, the particular circumstances under which either the one or the other of several methods deserves the preference.

Where the accuracy of an analytical method has been established already, in Section IV., no further statements are made on the subject here. Paragraphs of former Sections deserving particular attention are referred to in parentheses.

The extension of chemical science introduces almost every day new analytical methods of every description, which are, rightly or wrongly, preferred to the older methods; the present time may therefore be looked upon in this, as in so many other respects, as a period of transition, in which the new strives more than ever to overcome and supplant the old. I make this remark to show the impossibility of always adding to the description of a method an opinion of its usefulness and accuracy, and also to point out the importance, under such circumstances, of a proper systematic arrangement. I have in this Section generally arranged the various analytical methods upon the bases of their scientific principles, firmly persuaded that this will greatly tend to facilitate the study of the science, and will lead to endeavours to apply known principles to the separation of other bodies besides those to which they are already applied, or to apply new principles where experience has proved the old ones fallacious, and the methods based on them defective.

I conclude these introductory remarks, with the important caution to the student, *never to look upon a separation as successfully accomplished,* *before he has convinced himself, that the weighed precipitates, &c., are pure and more particularly free from those bodies from which it was intended to separate them.*

I. SEPARATION OF THE BASES FROM EACH OTHER.

FIRST GROUP.

POTASSA—SODA—AMMONIA—(LITHIA).*

§ 152.

Index:—The Nos. refer to those in the margin.

Potassa from soda, 1, 2, 6.
,, ammonia, 4, 5.
Soda from potassa, 1, 2, 6.
,, ammonia, 3, 4, 5.
Ammonia from potassa, 4, 5.
,, soda, 3, 4, 5.
(*Lithia* from the other alkalies, 7, 8, 9.)

1. *Methods based upon the different degrees of Solubility in Alcohol, of the Double Chlorides of the Alkali Metals and Bichloride of Platinum.*

a. Potassa from Soda.

It is an indispensable condition in this method that the two alkalies should exist in the form of chlorides. If, therefore, they are present in any other form, they must be first converted into chlorides, which in most cases may be effected by evaporation with hydrochloric acid in excess; in the case of nitrates the evaporation with hydrochloric acid must be repeated 4—6 times till the weight of the gently ignited mass ceases to diminish. In presence of sulphuric acid, phosphoric acid, and boracic acid, this simple method will not answer. For the methods of separating the alkalies from the two latter acids, and converting them into chlorides, see §§ 135 and 136. The presence of sulphuric acid being a circumstance of rather frequent occurrence, the way of meeting this contingency is given below (**2**). 1

Determine the total quantity of the chloride of sodium and chloride of potassium† (§§ 97, 98), dissolve in the least quantity of water, add to the fluid in a porcelain dish an excess of a strong aqueous solution of bichloride of platinum as neutral as possible. Enough platinum solution should be added to convert the sodium as well as the potassium into platinochloride. It is best to use a solution of known strength and to calculate roughly how much should be added. Evaporate on the water-bath nearly to dryness (the water in the bath should never actually boil and the double chloride of platinum and sodium should not lose its water of crystallization), treat the residue with alcohol of from ·86 to ·87 sp. gr., cover the dish with a glass plate, and allow to stand a few hours, with occasional stirring. If the supernatant fluid is not deep yellow, this is a proof that the quantity of bichloride of platinum used is insufficient. When the precipitate has settled, pour off the clear fluid through a weighed filter (preferably, an asbestos filter, § 97, 4, *a*) and examine the precipitate most minutely, if necessary with the aid of a microscope. If it is a heavy yellow powder (sufficiently magnified, small octahedral crystals) it is the pure chloride of platinum and potassium.* Then transfer it—best with the aid of the filtrate—to the filter, wash it with spirit of ·86 to ·87 sp. gr. and proceed according to § 97, 4 *a*. (Instead of weighing the double chloride or the platinum obtained from it, you may ignite gently in hydrogen, extract the chloride of potassium with water and weigh this or titrate the chlorine in it by § 141, I., *b*, *a*.) If, on the contrary, white saline particles (chloride of sodium) are to be seen mixed with the yellow crystalline powder, bichloride of platinum has been wanting, the whole of the chloride of sodium not having been completely converted into chloride of sodium and platinum. In this case the precipitate in the dish must be treated with some water, till all the chloride of sodium is dissolved, a fresh portion of bichloride of platinum is added, the whole evaporated nearly to dryness, and the above examination repeated. The quantity of the soda is usually estimated by subtracting from the united weight of the chloride of sodium and chloride of potassium the weight of the latter, calculated from that of the potassio-bichloride of platinum.

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* With regard to the separation of the oxides of cæsium and rubidium from the other alkalies, I refer to the "Analysis of Mineral Waters."

† Never take the weight of the alkaline chlorides without convincing yourself of their purity by dissolving them in water, which should give a clear solution, and testing the solution with ammonia and carbonate of ammonia, which must throw down no precipitate. It may be thought, perhaps, that a matter so simple need not be mentioned here; still I have found that neglect in this respect is by no means uncommon.

To make quite sure that the potassa has completely separated, it is advisable to add to the filtrate some water, some more bichloride of platinum, and, if the quantity of soda is only small, also some chloride of sodium; evaporate on the water-bath nearly to dryness, at a temperature not exceeding 75° (BISCHOF), and treat the residue in the manner just described. In order to diminish the solvent action of the spirit on the chloride of potassium and platinum, $\frac{1}{4}$ ether may be now mixed with it. Should this operation again leave a small undissolved residue of chloride of potassium and platinum, it is filtered off, best on a separate filter and first washed with alcohol and ether. As, however, this remainder of the double salt is generally impure, dissolve it on the filter with boiling water, evaporate with a few drops of bichloride of platinum, treat the residue with alcohol, and if any potassium salt remains determine it either with the principal quantity or by itself.

If you are not satisfied with an indirect estimation of the sodium, one of the following direct methods may be employed. *a.* Evaporate the filtrate till the spirit has gone off, dilute, digest the solution with small pure iron filings till the platinum is all thrown down, filter, add chlorine water till the protochloride of iron is converted into sesquichloride, precipitate with ammonia, filter off the hydrated sesquioxide of iron, and estimate the chloride of sodium in the filtrate. *β*. Evaporate the filtrate, finally in a porcelain crucible, to dryness, heat the residue to low redness in a current of hydrogen, extract with water, and determine the chloride of sodium in the solution. For small quantities of fluid this method will be found convenient. γ. A. MITSCHERLICH recommends to mix the filtrate with sulphuric acid, evaporate to dryness, ignite the residue, extract the sulphate of soda with water, and estimate it according to § 98, 1. These methods of course yield the soda salt in a pure condition only when the separation of the potash has been perfect. They present the advantage that the soda salt is brought under one's eyes and may be tested after weighing.

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* If small tesseral crystals are visible of a dark orange yellow color, and relatively large size, and appearing transparent by transmitted light, then the double chloride contains chloride of platinum and lithium (JENZSCH, Pogg. Ann. 104, 102).

Should the solution contain sulphuric acid, it may be in presence of hydrochloric acid or of some volatile acid, convert the alkalies first into neutral sulphates (§§ 97, 98), and weigh them as such. For the estimation of the potash one of the two following methods may be used. 2

α. First convert the sulphates into chlorides and then proceed as above. For this purpose baryta salts were formerly employed, or better an alcoholic solution of chloride of strontium. The sulphate of baryta, however, carries down considerable quantities of alkali salt, and the sulphate of strontia noticeable quantities, hence the employment of baryta more particularly cannot be recommended. H. ROSE advises repeated ignition of the alkaline sulphates with chloride of ammonium till the weight remains constant; this process is simple and well adapted for small quantities; no loss of alkali need be feared if the heat is not unnecessarily raised. L. SMITH advises the use of lead salts. Dissolve the alkaline sulphate, precipitate with pure neutral acetate of lead avoiding a large excess, add some alcohol, filter, precipitate the excess of lead with sulphuric acid, and evaporate to dryness with addition of sulphuric acid. This method when carefully conducted yields excellent results.

β. Precipitate the potash directly out of the solution of the sulphates. R. FINKENER* gives the following process. To the rather dilute solution of the salts in a capacious porcelain dish add bichloride of platinum in quantity more than sufficient to throw down all the potassium, evaporate on a water-bath down to a few c.c., allow to cool, add, at first in small quantities, 20 times the volume of a mixture of 2 parts absolute alcohol and 1 part ether, with stirring, filter after a short time and wash the precipitate with alcohol and ether till the washings are colorless. If when the alcohol and ether is first added, a strong aqueous solution of sulphate of soda separates, add some hydrochloric acid till the fluids mix. Dry the precipitate consisting of platinochloride of potassium and sulphate of soda, heat with the filter in a porcelain crucible till the filter is carbonized, then in a current of hydrogen to scarcely visible redness, extract the residue with hot water, ignite the platinum in the air, weigh and calculate from the weight the quantity of potassium.

The separation of potassium from sodium by bichloride of platinum gives results which are fully satisfactory and at all events far more exact than any method depending on another principle;

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* H. ROSE, Handbuch der anal. Chem. 6 Aufl. von FINKENER, ii. 923.

provided that the platinum solution is pure and the operations have been carefully performed in accordance with the directions. If you have any occasion to doubt the perfect purity of the weighed double salt you may always dissolve it in boiling water, evaporate with addition of a little platinum solution and reweigh the salt thus purified.

In the case of a series of analyses the potash in the separated double salt may be titrated. For this purpose triturate it with twice its quantity of pure oxalate of soda free from chlorides, heat the mixture to fusion in a platinum crucible, extract the residue with water, neutralize the filtrate nearly with acetic acid, titrate the chlorine in the alkaline chlorides (§ 141, I., *b*, *a*) and calculate 1 eq. potash for 3 eq. chlorine. Where the quantity of the double salt is very minute, moisten it and the filter with a strong solution of neutral oxalate of potash, allow to dry, ignite in a covered crucible and then proceed as above. If the separated platinum is weighed it will yield a good control (F. MOHR*).

b. AMMONIA FROM SODA.

The process is conducted exactly as in *a*, when the alkalies are present as chlorides. See also § 99, 2. If potassa also is present, the precipitate produced by bichloride of platinum is ammonio-bichloride of platinum + potassio-bichloride of platinum; in which case the weighed precipitate is cautiously ignited for a sufficient length of time, but not too strongly, until the chloride of ammonium is expelled, the gentle ignition continued in a stream of hydrogen or with addition of oxalic acid, the residue extracted with water, a few drops of hydrochloric acid added if oxalic acid was employed, and the chloride of potassium in the solution determined as directed § 97, 3. The weight found is calculated into potassio-bichloride of platinum, and the result deducted from the weight of the whole precipitate: the difference gives the ammonio-bichloride of platinum. The weighing of the separated platinum affords a good control. The method is seldom employed, as that given in 2 yields more exact results. 3

2. *Methods based upon the Volatility of Ammonia and its Salts.*

AMMONIA FROM SODA AND POTASSA.

a. The salts of the alkalies to be separated contain the same volatile acid, and admit of the total expulsion of their water by drying at 100°, *without losing ammonia* (*e.g.*, the chlorides). 4

Weigh the total quantity of the salts in a platinum crucible, and heat, with the lid on, gently at first, but ultimately for some time to faint redness; let the mass cool, and weigh. The decrease of weight gives the quantity of the ammonia salt. If the acid present is sulphuric acid, you must in the first place, take care to heat very gradually, as otherwise you will suffer loss from the decrepitation of the sulphate of ammonia: and, in the second place, bear in mind that part of the sulphuric acid of the sulphate of ammonia remains with the sulphates of the fixed alkalies, and that you must accordingly convert them into neutral salts, by ignition in an atmosphere of carbonate of ammonia, before proceeding to determine their weight (compare §§ 97 and 98). Chloride of ammonium cannot be separated in this manner from sulphates of the fixed alkalies, as it converts them, upon ignition, partly or totally into chlorides.

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* Zeitschr. f. anal. Chem. 12, 137.

b. Some one or other of the conditions given in a is not fulfilled.

If it is impracticable to alter the circumstances by simple means so as to make the method *a* applicable, the fixed alkalies and the ammonia must be estimated separately in different portions of the substance. The portion in which it is intended to determine the soda and potassa is gently ignited until the ammonia is completely expelled. The fixed alkalies are converted, according to circumstances, into chlorides or sulphates, and treated as directed in **1**, **2**, or **6**. The ammonia is estimated in another portion according to § 99, 3. **5**

3. *Indirect Methods.*

Of course, a great many of these may be devised; but the following is the only one in general use. **6**

POTASSA FROM SODA.

Convert both alkalies into neutral sulphates, or into chlorides (§§ 97 and 98), and weigh as such; estimate the sulphuric acid (§ 132) or chlorine (§ 141); and calculate the quantities of the soda and potassa from these data (see below, "Calculation of Analyses," § 200).*

The indirect method of determining potassa and soda is applicable only in the analysis of mixtures containing tolerably large quantities of both bases; but where this is the case, the process answers very well, affording also, more particularly, the advantage of expedition, if the chlorine in the weighed chlorides is titrated (§ 141, I., *b*).

Supplement to the First Group.

SEPARATION OF LITHIA FROM THE OTHER ALKALIES.

Lithia may be separated from *potassa* and *soda* in the indirect way, and by two direct methods:— **7**

a. Treat the nitrates or the chlorides, dried at 120°, with a mixture of equal volumes of absolute alcohol and anhydrous ether, digest at least for 24 hours, with occasional shaking (the salts must be completely disintegrated), decant rapidly on to a filter covering the funnel, and treat the residue again several times with smaller portions of the mixture of alcohol and ether. Determine, on the one part, the undissolved potassa and soda salts; on the other, the dissolved lithia salt, by distilling the fluid off, and converting the residue into sulphate. This method is apt to give too much lithium, as the potassa and soda salts, especially the chlorides, are not absolutely insoluble in a mixture of alcohol and ether. The results may be rendered more accurate by treating the impure lithia salt, obtained by distilling off the ether and alcohol, once more with alcohol and ether, with addition of a drop of nitric or hydrochloric acid, adding the residue left to the principal residue, and then converting the lithia salt into sulphate. If the salts, which it is intended to treat with alcohol and ether, have been ignited, however so gently, caustic lithia is formed—in the case of the chloride by the action of water—and carbonate of lithia by attraction of carbonic acid; in that case it is necessary, therefore, to add a few drops of nitric, or, as the case may be, hydrochloric acid, in the process of digestion. The separation of the chlorides of the alkali metals by a mixture of ether and spirit was originally recommended by RAMMELSBERG,[*] subsequently by JENZSCH.[†] This method cannot yield perfectly exact results, as the lithium salt obtained by evaporation of the spirituous solution is always found to be impure by the spectroscope (DIEHL[‡]).

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* Other methods are given by STOLBA (Zeitschr. f. anal. Chem. 2, 397) and MOHR (*Ib.* 7, 173).

If we have to separate the sulphates, they must be converted into nitrates or chlorides before they can be subjected to the above method. This conversion is best effected by means of lead salts, see **2**. Ignition with chloride of ammonium does not answer for sulphate of lithia, nor can the sulphuric acid be removed by baryta or strontia as the precipitated sulphates would contain lithia (DIEHL[§]).

b. Weigh the mixed alkalies, best in form of sulphates, and then determine the lithia as phosphate according to § 100. If the quantity of lithia is relatively very small, convert the weighed sulphates into chlorides (**7**), separate, in the first place, the principal amount of the potassa and soda by means of alcohol (§ 100), and then determine the lithia (MAYER[||]). **8**

c. When exact results are required the indirect method is to be preferred. Proceed first according to *a*, evaporate the spirituous solution of the chloride of lithium containing the remainder of the other chlorides to dryness, heat moderately, weigh, dissolve in water, estimate the chlorine, and calculate therefrom the lithium and sodium or potassium. BUNSEN[¶] also applied the method to the indirect estimation of lithia in presence of potassa and soda, by removing the silver from the filtrate, and separating the potassium with platinum. But I must here point out, that according to JENZSCH[**] the potassium double salt will contain lithium apparently in the form of the platinochloride of potassium and lithium. **9**

The sulphuric acid in weighed quantities of the sulphates of lithia, and of potassa or soda, cannot be estimated by baryta (see end of **7**).

The separation of lithia from *ammonia* may be effected like that of potassa and soda from ammonia (**4** and **5**).

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[*] Pogg. Annal. 66, 79.

[†] *Ib.* 104, 105.

[‡] Annal. d. Chem. u. Pharm. 121, 97.

[§] *Loc. cit.* p. 98.

[||] Annal. d. Chem. u. Pharm. 98, 193.

[¶] *Ib.* 122, 348.

[**] Pogg. Annal. 104, 102.

SECOND GROUP.

BARYTA—STRONTIA—LIME—MAGNESIA.

I. SEPARATION OF THE OXIDES OF THE SECOND GROUP FROM THOSE OF THE FIRST.

§ 153.

Index :—The Nos. refer to those in the margin.
Baryta from potassa and soda, 10, 12.
„ ammonia, 11.
Strontia from potassa and soda, 10, 13.
„ ammonia, 11.
Lime from potassa and soda, 10, 14.
„ ammonia, 11.
Magnesia from potassa and soda, 15—26.
„ ammonia, 11.

A. General Method.

1. THE WHOLE OF THE ALKALINE EARTHS FROM POTASSA AND SODA.

10 *Principle on which the method is based: Carbonate of ammonia precipitates, from a solution containing chloride of ammonium, only baryta, strontia, and lime.*

Mix the solution, in which the bases are assumed to be contained in the form of chlorides, with a sufficient quantity of chloride of ammonium to prevent the precipitation of the magnesia by ammonia; dilute rather considerably, add some ammonia, then carbonate of ammonia in slight excess, let the mixture stand covered for an hour in a moderately warm place, filter, and wash the precipitate with water to which a few drops of ammonia have been added.

The *precipitate* contains the *baryta, strontia,* and *lime;* the *filtrate* the *magnesia* and the *alkalies.* So at least we may assume in cases where the highest degree of accuracy is not required. Strictly speaking, however, the solution still contains exceedingly minute traces of lime and somewhat more considerable traces of baryta, as the carbonates of these two earths are not absolutely insoluble in a fluid containing chloride of ammonium; the precipitate also may contain possibly a little carbonate of ammonia and magnesia. Treat the precipitate according to § 154, and the filtrate—in rigorous analyses—as follows: Add 3 or 4 drops (but not much more) of dilute sulphuric acid, then oxalate of ammonia, and let the fluid stand again for 12 hours in a warm place. If a precipitate forms, collect this on a small filter, wash, and treat on the filter with some dilute hydrochloric acid, which dissolves the oxalate of lime, and leaves the sulphate of baryta undissolved. Since a little oxalate of magnesia may have separated with the former, add some ammonia to the hydrochloric solution, filter after the precipitate has settled, and mix the filtrate with the principal filtrate.

Evaporate the fluid containing the *magnesia* and the *alkalies* to dryness, and remove the ammonia salts by gentle ignition in a covered crucible, or in a small covered dish of platinum or porcelain.* In the residue, separate the magnesia from the alkalies by one of the methods given **15**—**24**.

2. THE WHOLE OF THE ALKALINE EARTHS FROM AMMONIA. **11** —The same principle and the same process as in the separation of potassa and soda from ammonia (**4** and **5**).

B. Special Methods.

SINGLE ALKALINE EARTHS FROM POTASSA AND SODA.

1. BARYTA FROM POTASSA AND SODA.

Precipitate the baryta with dilute sulphuric acid (§ 101, 1, *a*), **12** evaporate the filtrate to dryness, and ignite the residue, with addition towards the end of carbonate of ammonia (§ 97, 1 and § 98, 1). Take care to add a sufficient quantity of sulphuric acid to convert the alkalies also completely into sulphates. In exact analyses in order to save the alkaline salts adhering to the sulphate of baryta, remove the dry sulphate of baryta from the filter, heat it with a sufficient quantity of pure strong sulphuric acid to dissolve it completely, allow to cool, dilute largely, collect the sulphate of baryta (now almost absolutely pure) on the first filter, ignite, and weigh. Evaporate the filtrate in a platinum dish, drive off the sulphuric acid, and estimate the traces of the alkalies.

This method is, on account of its greater accuracy, preferable to the one in *A*, in cases where the baryta has to be separated only from one of the two fixed alkalies; but if both alkalies are present, the other method is more convenient, since the alkalies are then obtained as chlorides.

2. STRONTIA FROM POTASSA AND SODA.

Strontia may be separated from the alkalies, like baryta, by **13** means of sulphuric acid; but this method is not preferable to the one in **10**, in cases where the choice is permitted (comp. § 102).

3. LIME FROM POTASSA AND SODA.

Precipitate the lime with oxalate of ammonia (§ 103, 2, *b*, *a*), **14** evaporate the filtrate to dryness, and determine the alkalies in the ignited residue. In determining the alkalies, dissolve the residue, freed by ignition from the ammonia salts, in water, filter if necessary, acidify the filtrate, according to circumstances, with hydrochloric acid or sulphuric acid, and then evaporate to dryness; this treatment of the residue is necessary, because oxalate of ammonia partially decomposes chlorides of the alkali metals upon ignition, and converts the bases into carbonates, except in presence of a large proportion of chloride of ammonium. The results are still more accurate than in *A*, except where oxalate of ammonia has been used, after the precipitation by carbonate of ammonia, to remove the minute traces of lime from the filtrate.

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* This operation effects also the removal of the small quantity of sulphuric acid added to precipitate the traces of baryta, as sulphates of the alkalies are converted into chlorides upon ignition in presence of a large proportion of chloride of ammonium.

4. MAGNESIA FROM POTASSA AND SODA.*

a. Methods based upon the sparing solubility of Magnesia in Water.

α. Make a solution of the bases, as neutral as possible, and free from ammonia salts (it is a matter of indifference whether the acid is sulphuric, hydrochloric, or nitric), add baryta-water as long as a precipitate forms, heat to boiling, filter and wash the precipitate with boiling water. The precipitate contains the magnesia as hydrate. Dissolve it in hydrochloric acid, precipitate the baryta with sulphuric acid, and then the magnesia as ammonio-phosphate (§ 104, 2). The alkalies, which are contained in the solution, according to circumstances, as chlorides, nitrates, or caustic alkalies, are separated from the baryta as directed in **10** or **12**. LIEBIG, who was the first to employ this method, proposes crystallized sulphide of barium as precipitant. The method is not very exact, as magnesia is somewhat more soluble in solutions of alkali salts than in water. On this account the weighed alkali salt must always be tested for magnesia, and the latter estimated if required. 15

β. Precipitate the solution with a little pure milk of lime, boil, filter, and wash. Separate the lime and the magnesia in the precipitate according to **32**; the lime and the alkalies in the filtrate, according to **10** or **14**. This method may be employed when the magnesia has to be removed from a fluid containing lime and alkalies, provided the alkalies alone are to be determined. Minute quantities of magnesia also in this case remain with the alkali salt from the cause mentioned in *α*. 16

γ. Evaporate the solution of the chlorides (which must contain no other acids) to dryness, and, if chloride of ammonium is present, ignite; warm the residue with a little water (this will dissolve it with the exception of some magnesia, which separates). Add oxide of mercury shaken up with water, evaporate to dryness on the water-bath with frequent stirring, and proceed exactly as directed § 104, 3, *b*. There is no need to continue the ignition until the whole of the oxide of mercury is expelled; on the contrary, part of it may be filtered off together with the magnesia, and subsequently volatilized upon the ignition of the latter. Treat the residue with small quantities of hot water, filter off rapidly, and wash the magnesia with hot water, using small quantities at a time, and not continuing the operation unnecessarily. The solution contains the alkalies in form of chlorides. This method, proposed by BERZELIUS, gives satisfactory results, and, as far as my experience goes, is the best of those given under *a*. Take care to add the oxide of mercury only in proper quantity, and always test the alkaline chlorides for magnesia, a trace of which will generally be found. 17

δ. If the bases are present as chlorides, add *pure* oxalic acid† in sufficient quantity to convert all the bases present, viewed as potassa, into quadroxalates; add some water, evaporate to dryness in a platinum dish, and ignite. By this operation the chlorides of the alkali metals are partially, the chloride of magnesium completely, converted into oxalates, which, upon ignition, 18 give carbonated alkalies and magnesia. Treat the residue repeatedly with small quantities of boiling water; during this washing the precipitate may be transferred to the filter or remain in the dish, no matter which. When all the alkali salt is washed out, dry the filter, burn it in the dish, ignite strongly, and weigh the magnesia. If the solution looks a little turbid, evaporate to dryness, treat the residue with water, and filter off the trifling amount of magnesia still remaining; add, finally, hydrochloric acid to the filtrate, and determine the alkalies as chlorides.

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* The methods *a*, *α* and *β* are suitable for the separation of magnesia from lithia.

† SCHERER (Zeitschr. f. anal. Chem. 11, 197) recommends oxalate of ammonia instead.

19 If the bases are present in form of sulphates, add to the boiling solution chloride of barium, until the formation of a precipitate just ceases, evaporate the filtrate with an excess of oxalic acid, and proceed as in **18**. Remove the carbonate of baryta, which remains mixed with the magnesia, as directed **27**.

20 We owe these methods to MITSCHERLICH, and the description of them to LASCH.[*] I have not found the results particularly accurate. The weighed alkali salt should always be tested for magnesia. Usually a weighable precipitate is produced which cannot be passed over.[†]

The method described in **18** may also be successfully employed with nitrates, for which it is, indeed, specially recommended by DEVILLE.[‡] Carbonic acid and nitrous acid are evolved in the process of evaporation.

b. Methods based upon the Precipitation of Magnesia by Phosphate (or Arseniate) of Ammonia.

21 Add to the solution containing magnesia. potassa, and soda, ammonia in excess, and some chloride of ammonium, should this not be present already: precipitate the magnesia with *a slight excess* of pure phosphate of ammonia. Filter, remove the free ammonia by evaporation, and then precipitate the phosphoric acid with acetate of lead as a combination of phosphate and chloride of lead. Remove the excess of oxide of lead from the still hot fluid by ammonia and carbonate of ammonia, or by sulphuretted hydrogen, filter, and determine the potassa and soda in the filtrate as directed §§ 97 and 98 (O. L. ERDMANN,[§] HEINTZ[||]). A somewhat troublesome but very accurate method. If the solution contains much chloride of ammonium, the greater part must first be removed by volatilization.

22 The excess of phosphoric acid may be also removed with sesquioxide of iron or oxide of silver instead of with oxide of lead.

a. With sesquioxide of iron. Remove the ammonia by heat, neutralize if necessary with hydrochloric acid, add sesquichloride of iron till the fluid is yellowish, then add carbonate of ammonia till the fluid is neutral or only acid with carbonic acid, boil, filter off the basic phosphate of iron (which has a reddish-brown color, if enough sesquichloride has been used), wash, evaporate to dryness, expel the ammonia salts and estimate the potassa and soda according to §§ 97, 98. A good and convenient method.

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[*] Journ. f. prakt. Chem. 63, 343.

[†] I cannot recommend SONNENSCHEIN's method (boiling the chlorides with carbonate of silver); the filtrate always contains magnesia, and, indeed, more than mere traces.

[‡] Journ. f. prakt. Chem. 60, 17.

[§] *Ib.* 39, 278.

[||] Pogg. Annal. 73, 119.

β. With oxide of silver. Evaporate to dryness, ignite cautiously, dissolve in water and mix with nitrate of silver and a slight excess of carbonate of silver. Filter, remove the excess of silver by hydrochloric acid and evaporate the solution with excess of hydrochloric acid to dryness (CHANCEL[*]).

The separation is somewhat shorter, but less precise and also less convenient, if the magnesia is precipitated with arseniate (§ 127, 2) instead of phosphate of ammonia; in this case the filtrate is evaporated to dryness with chloride of ammonium and the residue ignited under a good chimney. The excess of arsenic acid volatilizes, while the alkalies remain as chlorides (always retaining, however, a little chloride of magnesium). C. v. HAUER[†] recommends a similar method.

c. Method based on the Precipitation of the Magnesia as Carbonate of Ammonia and Magnesia.

23 Mix the solution of sulphates, nitrates, or chlorides (it must be very concentrated) with an excess of a concentrated solution of sesquicarbonate of ammonia in water and ammonia (230 grm. of the salt, 360 c.c. solution of ammonia sp. gr. ·96, and water to 1 litre). After twenty-four hours filter off the precipitate ($MgO,CO_2 + NH_4O,CO_2 + 4$ aq.), wash it with the solution of caustic and carbonated ammonia used for the precipitation, dry, ignite strongly and for a sufficient length of time, and weigh the magnesia. Evaporate the filtrate to dryness, keeping the heat at first under 100°, expel the ammonia salts, and determine the alkalies as chlorides or sulphates. When soda alone is present the results are tolerably satisfactory. In the presence of potassa the ignited magnesia must be extracted with water, before weighing, as it contains an appreciable quantity of carbonate of potassa; the washings are to be added to the principal filtrate. This last measure is unnecessary in the absence of potassa. The magnesia is always a little too low. Mean error $\frac{9}{1000}$ (F. G. SCHAFFGOTSCH,[‡] H. WEBER[§]).

d. Method depending on the precipitation of the alkalies as silicofluorides (STOLBA[||]).

24 Where you have a mixture of the chlorides of potassium and magnesium or of the nitrates of potassa and magnesia, you may estimate the potassium in one aliquot part as silicofluoride (§ 97, 5) and precipitate the magnesium in another as ammonio-phosphate (§ 104, 2). If you want to make both estimations in the same portion of fluid, take the filtrate from the silicofluoride of potassium, remove the excess of hydrofluosilicic acid with alcoholic solution of acetate of potash, washing with a mixture of alcohol and water in equal volumes, and estimate the magnesia in the filtrate. If you have the sulphates to analyse, the method cannot, in my opinion, be trusted on account of the difficult solubility of sulphate of magnesia in dilute alcohol.

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[*] Comp. rend. 50, 94.

[†] Jahrb. der k.k. geolog. Reichsanstalt, 4, 863.

[‡] Pogg. Annal. 104, 482.

[§] Vierteljahresschrift f. prakt. Pharm. 8, 161.

[||] Zeitschr. f. anal. Chem. 4, 160.

This method is less adapted to the separation of soda from magnesia as silicofluoride of sodium is more soluble in spirit than the potassium salt. In the case of sulphates the method must be rejected; in the case of chlorides or nitrates, add 2 volumes of strong alcohol after the hydrofluosilicic acid, and allow to settle completely before filtering.

c. Indirect methods, which give at the same time the quantity of potassa and soda, if both are present.

α. Weigh the sulphates, divide the solution into two parts, in one estimate the magnesia (§ 104, 2), in the other the potassa (**2**), calculate the sulphate of magnesia and the sulphate of potassa, and find the sulphate of soda from the difference. **25**

β. Convert, with proper care, the bases into pure neutral sulphates, weigh, dissolve in water, and determine the sulphuric acid by chloride of barium (§ 132); precipitate the excess of baryta from the filtrate by sulphuric acid, filter again, concentrate the filtrate by evaporation, and determine the magnesia as directed § 104, 2 (K. List*). **26**

Calculate the magnesia found into sulphate, and deduct this from the total weight of the sulphates: the difference shows the quantity of the alkaline sulphates; deduct also the sulphuric acid combined with the magnesia from the total quantity of sulphuric acid: the difference gives the amount combined with the alkalies. See **6**.

It will be readily understood that good results cannot be expected from these indirect methods unless the greatest care is used. The tendency of sulphate of baryta to carry down soluble salts interferes with the accuracy of *β*.

II. SEPARATION OF THE OXIDES OF THE SECOND GROUP FROM EACH OTHER.

§ 154.

Index —The Nos. refer to those in the margin.

Baryta from strontia, 28, 31, 40.
,, lime, 30, 31, 35, 40.
,, magnesia, 27, 29.
Strontia from baryta, 28, 31, 40.
,, lime, 34, 38, 39
,, magnesia, 27, 29.
Lime from baryta, 28, 30, 31, 35, 40.
,, strontia, 34, 38, 39.
,, magnesia, 27, 32, 33, 36, 37.†
Magnesia from baryta, 27, 29
,, strontia, 27, 29.
,, lime, 27, 32, 33, 36, 37.†

A. *General Method.*

THE WHOLE OF THE ALKALINE EARTHS FROM EACH OTHER.

27 Proceed as in **10**. The magnesia is precipitated from the filtrate as ammonio-phosphate (see p. 421, foot note). The precipitated carbonates of the baryta, strontia, and lime, are dissolved in hydrochloric acid, and the bases separated as directed in **28**. The traces of magnesia, which may be present in the carbonate of ammonia precipitate, are obtained by evaporating the filtrate from the sulphate of strontia or lime to dryness, taking up the residue with water and precipitating the solution with ammonia and phosphate of soda and ammonia.

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* Annal. d. Chem. u. Pharm. 81, 117.

† Compare the method of OEFFINGER, Zeitschr. f. anal. Chem. 8, 456.

B. *Special Methods.*

1. *Methods based upon the Insolubility of Silicofluoride of Barium.*

BARYTA FROM STRONTIA AND FROM LIME.

28 Mix the neutral or slightly acid solution with hydrofluosilicic acid* in excess, add one-third of the volume of alcohol of ·81 sp. gr., let the mixture stand twelve hours, collect the precipitate of *silicofluoride of barium* on a weighed filter, wash with a mixture of equal parts of water and alcohol, until the washings cease to show even the least trace of acid reaction (but no longer), and dry at 100°. Precipitate the strontia or lime from the filtrate by dilute sulphuric acid (§ 102, 1, *a*, and § 103, 1). The results are satisfactory. For the properties of silicofluoride of barium, see § 71. If both strontia and lime are present, the sulphates are weighed, and then separated according to **34**, or they are converted into carbonates (§ 132, II., *b*), and separated according to **38** or **39**.

2. *Methods based upon the Insolubility of Sulphate of Baryta, or Sulphate of Strontia, as the case may be, in water and in Solution of Hyposulphite of Soda.*

a. BARYTA AND STRONTIA FROM MAGNESIA.

29 Precipitate the baryta and strontia with sulphuric acid (§ 101, 1, *a* and § 102, 1, *a*), and the magnesia from the filtrate with ammonia and double phosphate of soda and ammonia (§ 104, 2).

b. BARYTA FROM LIME:

30 Mix the solution with hydrochloric acid, then with highly dilute sulphuric acid (1 part acid to 300 water), as long as a precipitate forms; allow to deposit, and determine the sulphate of baryta as directed § 101, 1, *a*. Concentrate the washings by evaporation, and add them to the filtrate, neutralize the acid with ammonia, and precipitate the lime as oxalate (§ 103, 2, *b*, *a*). The method is principally to be recommended when small quantities of baryta have to be separated from much lime. If we have to separate sulphate of lime from sulphate of baryta the salts may (in the absence of free acids) be treated repeatedly with a solution of hyposulphite of soda at a gentle heat. The sulphate of baryta remains undissolved, the sulphate of lime dissolves. The lime is precipitated from the filtrate by oxalate of ammonia (DIEHL†).

3. *Method based upon the different deportment with Carbonated Alkalies of Sulphate of Baryta on the one hand, and Sulphates of Strontia and Lime on the other.*

BARYTA FROM STRONTIA AND LIME.

31 Digest the precipitated sulphates of the three bases for twelve hours at the common temperature (15°—20°), with frequent stirring, with a solution of carbonate of ammonia, decant the fluid on to a filter, treat the residue repeatedly in the same way, wash finally with water, and in the still moist precipitate, separate the undecomposed sulphate of baryta by means of cold dilute hydrochloric acid from the carbonates of strontia and lime formed. To hasten the separation you may boil the sulphates for some time with a solution of carbonate of potassa (not soda) to which ⅓ the amount of the carbonate, or more, of sulphate of potassa has been added. By this process also the sulphates of strontia and lime are decomposed, the sulphate of baryta remaining unacted on. If the bases are in solution, the above solution of carbonate and sulphate of potassa is added in excess at once, and the whole boiled. The precipitate, consisting of sulphate of baryta and carbonates of strontia and lime, is to be treated as above with cold hydrochloric acid (H. Rose*).

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* If not kept in a gutta-percha bottle it should be freshly prepared.

† Journ. f. prakt. Chem. 79, 430.

4. *Methods based on the Insolubility of Sulphate of Lime in Spirit of Wine.*

LIME FROM MAGNESIA.

32 *a.* Dissolve the bases as chlorides, remove the water by evaporation, dissolve the residue in strong (but not absolute) alcohol, add a slight excess of pure strong sulphuric acid, digest in the cold, allow to stand for some hours, transfer the precipitate consisting of sulphate of lime and some sulphate of magnesia to a filter, wash away the acid thoroughly with nearly absolute alcohol, and then continue the washing with alcohol sp. gr. ·96—·95 till a few drops of the washings give no residue on evaporation. Weigh the sulphate of lime according to § 103, 1. Evaporate the alcohol from the filtrate, and estimate the magnesia according to § 104, 2. The method is in itself not new, but A. CHIZYNSKI,† adopting the precautions here given, has obtained excellent results, even in the presence of phosphoric acid.

33 *b.* SMALL QUANTITIES OF LIME FROM MUCH MAGNESIA. Convert the bases into neutral sulphates, dissolve the mass in water, and add alcohol with constant stirring, till a slight permanent turbidity is produced. Wait a few hours and then filter, wash the precipitated sulphate of lime with alcohol which has been diluted with an equal volume of water, and determine it after § 103, 1, *a* (in which case the weighed sulphate must be tested for magnesia), or dissolve the precipitate in water containing hydrochloric acid and separate the lime from the small quantity of magnesia possibly coprecipitated according to **36** (SCHEERER‡).

5. *Methods based on the Insolubility of Sulphate of Strontia and Baryta in solution of Sulphate of Ammonia.*

34 STRONTIA FROM LIME. If the mixture is soluble, dissolve in the smallest quantity of water, add about 50 times the quantity of the substance of sulphate of ammonia dissolved in four times its weight of water, and either boil for some time with renewal of the

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* Pogg. Annal. 95, 286, 299, 427.

† Zeitschr. f anal. Chem. 4, 348.

‡ Annal. d. Chem. u. Pharm. 110, 237.

water that evaporates and addition of a very little ammonia (as the solution of sulphate of ammonia becomes acid on boiling), or allow to stand at the ordinary temperature for twelve hours. Filter and wash the precipitate, which consists of sulphate of strontia and a little sulphate of strontia and ammonia, with a concentrated solution of sulphate of ammonia till the washings remain clear on addition of oxalate of ammonia. The precipitate is cautiously ignited, moistened with a little dilute sulphuric acid (to convert the small quantity of sulphide of strontium into sulphate), reignited and weighed. The highly dilute filtrate is precipitated with oxalate of ammonia, and the lime determined according to § 103, 2, *b*, *a*. If you have the solid sulphates to analyse, they are very finely powdered and boiled with concentrated solution of sulphate of ammonia with renewal of the evaporated water and addition of a little ammonia. Results very close, *e.g.*, 1·048 SrO,NO_5 instead of 1·053, and ·497 CaO,CO_2, instead of ·504 (H. ROSE*).

BARYTA may be separated FROM LIME in the same way. 35

6. *Methods based upon the Insolubility of Oxalate of Lime in Chloride of Ammonium and in Acetic Acid.*

LIME FROM MAGNESIA.

a. Mix the properly diluted solution with sufficient chloride of 36
ammonium to prevent the formation of a precipitate by ammonia, which is added in slight excess; add oxalate of ammonia as long as a precipitate forms, then a further portion of the same reagent, about sufficient to convert the magnesia also into oxalate (which remains in solution). This excess is absolutely indispensable to insure complete precipitation of the lime, as oxalate of lime is slightly soluble in chloride of magnesium not mixed with oxalate of ammonia (Expt. No. 83). Let the mixture stand twelve hours, decant the supernatant clear fluid, as far as practicable, from the precipitated oxalate of lime, mixed with a little oxalate of magnesia, on to a filter, wash the precipitate once in the same way by decantation, then dissolve in hydrochloric acid, add water, then ammonia in slight excess, and a little oxalate of ammonia. Let the fluid stand until the precipitate has completely subsided, then pour on to the previous filter, transfer the precipitate finally to the latter, and proceed exactly as directed § 103, 2, *b*, *a*. The first filtrate contains by far the larger portion of the magnesia, the second the remainder. Evaporate the second filtrate, acidified with hydrochloric acid, to a small volume, then mix the two fluids, and precipitate the magnesia with double phosphate of soda and ammonia† as directed § 104, 2. If the quantity of ammonia salts present is considerable, the estimation of the magnesia is rendered more accurate by evaporating the fluids, in a large platinum or porcelain dish to dryness, and igniting the residuary saline mass, in small portions at a time, in a smaller platinum dish, until the ammonia salts are expelled. The residue is then treated with hydrochloric acid and water, warmed, allowed to cool, and rendered just alkaline with ammonia. If enough

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* Pogg. Annal. 110, 296.

† This is preferable to phosphate of soda as a precipitant, see MOHR, Zeitschr. f. anal. Chem. 12, 36.

chloride of ammonium is present, no hydrate of magnesia will fall down, but occasionally small flocks of silica or alumina are to be seen. Filter them off and finally precipitate with ammonia and double phosphate of soda and ammonia. If the precipitate produced by ammonia is at all considerable dissolve it in hydrochloric acid, evaporate the solution on a water-bath to dryness, treat the residue with hydrochloric acid and water, render alkaline with ammonia, filter and add the filtrate to the principal solution.

Numerous experiments have convinced me that this method, which is so frequently employed, gives accurate results only if the foregoing instructions are strictly complied with. It is only in cases where the quantity of magnesia present is relatively small, that a single precipitation with oxalate of ammonia may be found sufficient (comp. Expt. No. 84*).

b. In the case of lime and magnesia combined with phosphoric acid, dissolve in the least possible quantity of hydrochloric acid, add ammonia until a copious precipitate forms; redissolve this by addition of acetic acid, and precipitate the lime with an excess of oxalate of ammonia. To determine the magnesia, precipitate the filtrate with ammonia and double phosphate of soda and ammonia. As free acetic acid by no means prevents the precipitation of small quantities of oxalate of magnesia, the precipitate contains some magnesia, and, as oxalate of lime is not quite insoluble in acetic acid, the filtrate contains some lime; these two sources of error compensate each other in some measure. In accurate analyses, however, these trifling admixtures of magnesia and lime are afterwards separated from the weighed precipitates of carbonate of lime and pyrophosphate of magnesia respectively. 37

7. *Method based upon the Insolubility of Nitrate of Strontia in Alcohol and Ether.*

STRONTIA FROM LIME (*after* STROMEYER).

Digest the perfectly dry nitrates in a closed flask with absolute alcohol, to which an equal volume of ether should be added (H. ROSE). Filter off the undissolved nitrate of strontia in a covered funnel, wash with the mixture of alcohol and ether, dissolve in water, and determine as sulphate of strontia (§ 102, 1). Precipitate the lime from the filtrate by sulphuric acid. The results are satisfactory. 38

8. *Indirect Method.*

STRONTIA FROM LIME.

Determine both bases first as carbonates, precipitating them either with carbonate or with oxalate of ammonia (§§ 102, 103); then estimate the amount of carbonic acid in them, and calculate the amount of strontia and of lime as directed in § 200. The determination of the carbonic acid may be effected by fusion with vitrified borax (§ 139, II., *c*), but the application of a moderate 39 white heat, such as is given by a good gas blowpipe without the use of a crucible jacket, is alone sufficient to drive out all the carbonic acid from both the carbonates (F. G. SCHAFFGOTSCH*). I can strongly recommend this method. It is well to precipitate the carbonates hot, to press the precipitate cautiously down in the platinum crucible and turn over the agglomerated cake every now and then till, after repeated ignitions, the weight has become constant. The results are good, if neither of the bases is present in too minute quantity.

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* Further experiments will be found in Zeitschr. f. anal. Chem. 7, 310. Compare also WITTSTEIN, Zeitschr. f. anal. Chem. 2, 318, and COSSA, *Ib.* 8, 141. According to HAGER, *Ib.* 9, 254, the precipitate of oxalate of lime will be free from magnesia if filtered off immediately; however, I fear that a little lime might in this case be left in solution.

The indirect separation may of course be effected by means of other salts, and can be used also for the determination of LIME IN PRESENCE OF BARYTA or of BARYTA IN PRESENCE OF STRONTIA. In the expulsion of carbonic acid from carbonate of baryta vitrified borax must be used (§ 139, II., *c*). **40**

THIRD GROUP.

ALUMINA—SESQUIOXIDE OF CHROMIUM.

I. SEPARATION OF THE OXIDES OF THE THIRD GROUP FROM THE ALKALIES.

§ 155.

1. FROM AMMONIA.

a. Salts of alumina and of sesquioxide of chromium may be separated from salts of ammonia by ignition. However, in the case of alumina, this method is applicable only in the absence of chlorine (volatilization of chloride of aluminum). The safest way, therefore, is to mix the compound with carbonate of soda before igniting. **41**

b. Determine the ammonia by one of the methods given in § 99, 3, using solution of potassa or soda to effect the expulsion of the ammonia. The alumina and sesquioxide of chromium are then determined in the residue in the same way as in **43**. **42**

2. FROM POTASSA AND SODA.

a. Precipitate and determine the sesquioxide of chromium and alumina with ammonia as directed in § 105, *a*, and § 106, 1, *a*. The filtrate contains the alkalies, which are then freed from the salt of ammonia formed, by evaporation to dryness and ignition. In the presence of large quantities of alkali salts it is well to dissolve the moderately ignited precipitate in hydrochloric acid, and reprecipitate with ammonia. **43**

b. *Alumina* may be separated also from potassa and soda, by heating the nitrate (see **46**). **44**

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* Pogg. Annal. 113, 615.

II. SEPARATION OF THE OXIDES OF THE THIRD GROUP FROM THE ALKALINE EARTHS.

§ 156.

Index:—The Nos. refer to those in the margin.

Alumina from baryta, 45—50, and 51.
„ strontia, 45—50, and 51.
„ lime, 45—50, and 52, 53, 54.
„ magnesia, 45—50, and 53, 54.
Sesquioxide of chromium from the alkaline earths, 55—58.

a. SEPARATION OF ALUMINA FROM THE ALKALINE EARTHS.

A. *General Methods.*

THE WHOLE OF THE ALKALINE EARTHS FROM ALUMINA.

1. *Method based upon the Precipitation of Alumina by Ammonia, and upon its Solution in Soda.*

Put the solution in a platinum dish or, with less advantage, 45 a porcelain dish. Let it be dilute and warm. Add a tolerable quantity of chloride of ammonium, if such be not already present, then very gradually, almost drop by drop (WRINKLE[*]), ammonia as free as possible from carbonic acid, in moderate excess, and boil till no more free ammonia is observable. Under these circumstances, a little magnesia, and also a small quantity of carbonate of lime, baryta, or strontia are at first precipitated along with the alumina; on the boiling with chloride of ammonium, the coprecipitated alkaline earths redissolve, so that the alumina finally retains only an unweighable or scarcely weighable trace of magnesia, &c. Allow to deposit, and proceed with the alumina determination according to § 105, *a*. In very exact analysis it is well, after moderately washing the alumina precipitate, to redissolve it in hydrochloric acid, and reprecipitate with ammonia as above. In separations of alumina from lime or magnesia this double precipitation is especially necessary in the presence of sulphates. After the alumina has been weighed fuse it for a long time with bisulphate of potassa, dissolve the fused mass in water, and determine any silicic acid[†] that may remain. The solution, when mixed with potassa in excess, will often not appear perfectly clear, but will contain a few flocks of magnesia (perhaps also traces of carbonate of lime, baryta, or strontia). If there is any amount of the latter, filter it off, dissolve in nitric acid, precipitate with ammonia, boil till the fluid ceases to smell of ammonia, filter, evaporate the small quantity of fluid in a platinum capsule, ignite, weigh the residual magnesia (which may contain traces of other alkaline earths), deduct it from the alumina, dissolve it in hydrochloric acid, and add to the original filtrate. In order to the further separation of the alkaline earths, acidify the fluid containing them with hydrochloric acid, evaporate (preferably in a platinum dish) to a small bulk, and while still warm add ammonia just in excess. A small precipitate of alumina is sometimes formed at this stage; filter off, wash and weigh with the principal precipitate. In the filtrate determine the alkaline earths according to § 154.

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[*] Zeitschr. f. anal. Chem. 10, 96.

[†] A small quantity will always be found if you have boiled in a glass or porcelain

Instead of precipitating the alumina as directed you may add ammonia in moderate excess to the boiling hot solution, boil for two minutes, acidify distinctly with acetic acid, heat again for a few minutes, add ammonia till very slightly alkaline, and then proceed as above.*

2. *Method based upon the unequal Decomposability of the Nitrates at a Moderate Heat* (DEVILLE†).

To make this simple and convenient method applicable, the bases must be present as pure nitrates. Evaporate to dryness in a platinum dish, and heat gradually, with the cover on, in the sand- or air-bath—or, better still, on a thick iron disk, with two cavities, one for the platinum dish, the other, filled with brass turnings, for the thermometer (comp. § 31)—to from 200° to 250°, until a glass rod moistened with ammonia ceases to indicate further evolution of nitric acid fumes. You may also, without risk, continue to heat until nitrous acid vapors form. The residue consists of alumina, nitrates of baryta, strontia, and lime, and nitrate and basic nitrate of magnesia. **46**

Moisten the mass with a concentrated solution of nitrate of ammonia, and heat gently, but do not evaporate to dryness. Repeat this operation until no further evolution of ammonia is perceptible. (The basic nitrate of magnesia, insoluble in water, dissolves in nitrate of ammonia, with evolution of ammonia, as neutral nitrate of magnesia.) Add water, and digest at a gentle heat.

> If the nitrate of ammonia has evolved only imperceptible traces of ammonia, pour hot water into the dish, stir, and add a drop of dilute ammonia; this must cause no turbidity in the fluid; should the fluid become turbid, this proves that the heating of the nitrates has not been continued long enough; in which case you must again evaporate the contents of the dish, and heat once more.

The alumina remains undissolved in the form of a dense granular substance. Decant after digestion, and wash with boiling water; ignite strongly in the same vessel in which the separation has been effected, and weigh. Test the weighed alumina according to **45**. Separate the alkaline earths as directed § 154.

In the same way alumina may be separated also from potassa and soda (**44**).

3. *Method in which the processes of* 1 *and* 2 *are combined.*

Precipitate the alumina as in **45**, wash in the same way as there directed, then treat while still moist with nitric acid, and proceed according to **46** to remove the trifling amount of magnesia, &c., coprecipitated; add the solution obtained to the principal solution of the alkaline earths, and treat the fluid as directed in **45**. This method may be employed also in the case of chlorides; it will be sometimes found useful. **47**

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* Handb. der anal. Chem. v. H. ROSE, 6 Aufl. von FINKENER, ii. 647.

† Journ. f. prakt. Chem. 1853, 60, 9.

4. *Method based upon the Precipitation of Alumina by Acetate or Formiate of Soda upon boiling.*

The same process as for the separation of sesquioxide of iron from the alkaline earths. The method is employed more particularly when both alumina and sesquioxide of iron have to be separated from alkaline earths at the same time. The precipitation of the alumina is usually not quite thorough, so that it will be necessary to separate the dissolved alumina from the filtrate (**45**). **48**

5. *Method based on the Precipitation of Alumina by Succinate of Ammonia.*

Proceed as for the precipitation of sesquioxide of iron by the same reagent (§ 159); especially to be employed, when alumina and sesquioxide of iron are both to be separated from alkaline earths at the same time. The filtrate must be tested according to **48**. **49**

6. *Method based upon the Formation of a Soluble Alkaline Aluminate in the dry way.*

See § 161. **50**

B. *Special Methods.*

SOME OF THE ALKALINE EARTHS FROM ALUMINA.

1. *Methods based upon the Precipitation of some of the Salts of the Alkaline Earths.*

a. BARYTA AND STRONTIA FROM ALUMINA.

Precipitate the baryta and strontia with *sulphuric acid* (§§ 101 and 102), and the alumina from the filtrate as directed § 105, *a*. This method is especially suited for the separation of baryta from alumina. In accurate analyses the sulphate of baryta must be purified according to **12**. **51**

b. LIME FROM ALUMINA.

Add ammonia to the solution until a permanent precipitate forms, then acetic acid until this precipitate is redissolved, then acetate of ammonia, and finally *oxalate of ammonia* in slight excess (§ 103, 2, *b*, *β*); allow the precipitated oxalate of lime to deposit in the cold, then filter, and precipitate the alumina from the filtrate as directed § 105, *a*. Compare § 161, 4, *b*. **52**

c. MAGNESIA AND SMALL QUANTITIES OF LIME FROM ALUMINA.

Mix with some tartaric acid, supersaturate with ammonia and from the clear fluid (in the presence of enough alumina no tartrate of lime is precipitated) precipitate first the lime by oxalate of ammonia, then the magnesia by double phosphate of soda and ammonia. If the alumina is to be determined in the filtrate, the latter must be evaporated with addition of carbonate of soda and nitre to dryness, the residue ignited, softened with water, dissolved in hydrochloric acid (not in the platinum dish), and the alumina precipitated by ammonia. The ammonio-phosphate of magnesia which may contain basic tartrate of magnesia is to be dissolved in hydrochloric acid, reprecipitated with ammonia, with addition of some double phosphate of soda and ammonia, then dried, ignited, and weighed. **53**

2. *Method based upon the Precipitation of Alumina by Carbonate of Baryta.*

ALUMINA FROM MAGNESIA AND SMALL QUANTITIES OF LIME.

Mix the slightly acid dilute fluid in a flask, with a moderate **54** excess of carbonate of baryta shaken up with water; cork the flask and let the mixture stand in the cold until the hydrated alumina has subsided, wash by decantation three times, filter, and then determine the alumina in the precipitate as directed **51**; in the filtrate, first precipitate the baryta by sulphuric acid (**30**), and then separate the lime and magnesia according to § 154.

b. SEPARATION OF SESQUIOXIDE OF CHROMIUM FROM THE ALKALINE EARTHS.

1. The best way to separate THE WHOLE OF THE ALKALINE EARTHS from sesquioxide of chromium at the same time is to convert the latter into chromic acid. This may be done in the dry or the wet way.

a. Dry way. Mix the powdered substance with about 8 times **55** its weight of a mixture of 2 parts of carbonate of soda and 1 part of nitre, and fuse in a platinum crucible. On treating the fused mass with hot water, the chromium dissolves as alkaline chromate (to be estimated according to § 130), while the alkaline earths remain in the residue as carbonates or in the caustic state (magnesia). If the residue is not perfectly white, extract the remainder of the chromic acid from it by boiling with solution of carbonate of soda.

b. Wet way. Suitable for separating chromium from baryta, **56** strontia, and lime.

α. Nearly neutralize the acid fluid with carbonate of soda, add excess of acetate of soda, warm and pass chlorine, adding carbonate of soda occasionally to keep the fluid nearly neutral. As soon as all the chromium is oxidized, precipitate with carbonate of soda by the aid of heat, and proceed for the rest according to **55** (GIBBS*). Bromine instead of chlorine may be used; however, the oxidation is but tardily effected by the mere addition of bromine water.

β. Neutralize the solution with carbonate of soda, add hypochlorite of soda and heat, adding more hypochlorite if necessary till all the sesquioxide of chromium is converted. Add now more carbonate of soda, heat, decant through a filter, boil the residue again with carbonate of soda, and proceed according to **55**.

2. SESQUIOXIDE OF CHROMIUM FROM BARYTA, STRONTIA, **57** AND LIME. To separate baryta and strontia, precipitate the moderately acid, hot, dilute solution with sulphuric acid—in the presence of strontia, allow to cool and add alcohol—and when the precipitate has settled, filter. Sesquioxide of chromium cannot be separated by ammonia from the alkaline earths, since, even though carbonic acid be completely excluded, particles of the alkaline earths are thrown down with the sesquioxide of chromium. From solutions containing a salt of sesquioxide of chromium, lime cannot be precipitated completely by oxalate of ammonia; but it may be by sulphuric acid and alcohol (§ 103, 1).

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* Zeitschr. f. anal. Chem. 3, 328.

3. **Sesquioxide of chromium** may also be separated from **magnesia** and small quantities of **lime** by means of carbonate of baryta. See **54**. 58

III. Separation of Sesquioxide of Chromium from Alumina.*

§ 157.

a. Fuse the oxides with 2 parts of nitrate of potassa and 4 parts of carbonate of soda in a platinum crucible, treat the fused mass with boiling water, rinse the contents of the crucible into a porcelain dish or beaker, add a somewhat large quantity of chlorate of potassa, supersaturate slightly with hydrochloric acid, evaporate to the consistence of syrup, and add, during the latter process, some more chlorate of potassa in portions, to remove the free hydrochloric acid. Dilute now with water, and separate the alumina and sesquioxide of chromium as directed § 130, II., *c*, *a*. If you omit the evaporation with hydrochloric acid and chlorate of potassa, part of the chromic will be reduced by the nitrous acid in the fluid, and sesquioxide of chromium will accordingly, upon addition of ammonia, precipitate with the alumina (Dexter†). 59

b. Dissolve the oxides in hydrochloric acid, add soda or potassa solution in sufficient excess and saturate the clear green solution with chlorine gas. The sesquioxide of chromium will be converted into chromic acid, and the alumina partially separated. When the fluid has become of a pure yellow color, heat to remove the excess of chlorine, add carbonate of ammonia, and digest to destroy the hypochlorous acid and precipitate the still dissolved alumina, and proceed according to § 130, II., *c*, *a* (Wöhler‡). 60

c. Nearly neutralize the acid solution with carbonate of soda, add acetate of soda in excess, pass chlorine or add bromine and warm. The sesquioxide of chromium will readily be converted into chromic acid, especially if carbonate of soda is added every now and then to keep the fluid nearly neutral. As soon as this is effected proceed according to § 130, II., *c*, *a* (Gibbs§). 61

FOURTH GROUP.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—SESQUIOXIDE OF IRON—(SESQUIOXIDE OF URANIUM).

I. Separation of the Oxides of the Fourth Group from the Alkalies.

§ 158.

A. *General Methods.*

1. All the Oxides of the Fourth Group from Ammonia.

Proceed as for the separation of sesquioxide of chromium and alumina from ammonia, **41**. It must be borne in mind that the 62 oxides of the fourth group comport themselves, upon ignition with chloride of ammonium, as follows:—Sesquioxide of iron is partly volatilized as sesquichloride; the oxides of manganese are converted into protochloride of manganese containing protoxide with volatilization of some protochloride;[*] the oxides of nickel and cobalt are reduced to the metallic state, no chloride being lost by volatilization;[†] oxide of zinc volatilizes, as chloride. It is, therefore, generally the safest way to add carbonate of soda. The ammonia is determined in a separate portion.

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* The separation of alumina from titanic acid will be given under the Analysis of Silicates.

† Pogg. Annal. 89, 142.

‡ Annal. d. Chem. u. Pharm. 106, 121.

§ Zeitschr. f. anal. Chem. 3, 327.

2. All Oxides of the Fourth Group from Potassa and Soda.

63 Mix the solution in a flask with chloride of ammonium if necessary, add ammonia till neutral or slightly alkaline, then yellow sulphide of ammonium saturated with sulphuretted hydrogen, fill the flask nearly to the top with water, cork it, allow the precipitated sulphides to subside, and then filter them off from the fluid containing the alkalies. In performing this process the precautionary rules given under the heads of the several metals in question (§§ 108—113) must be borne in mind.[‡] (If notwithstanding, the filtrate is brownish, acidify it with acetic acid, pass sulphuretted hydrogen, boil and filter off the small quantity of the sulphide of nickel which then separates.) Acidify the filtrate with hydrochloric acid, evaporate, filter off the sulphur, if necessary, continue the evaporation to dryness, ignite the residue to remove the ammonia salts, and determine the alkalies by the methods given § 152.

B. *Special Methods.*

64
1. Oxide of Zinc from Potassa and Soda, by precipitating the zinc from the solution of the acetates with sulphuretted hydrogen (see **87**).
2. Protoxide of Nickel and Protoxide of Cobalt from the Alkalies, by igniting the chlorides in a stream of hydrogen and treating the residue with water. By precipitating the alkalies as silicofluorides (§ 97, 5. Stolba[§]); less suitable for soda than potassa.
3. Sesquioxide of Iron from Potassa and Soda, by precipitating the sesquioxide of iron with ammonia; or by heating the nitrates (see **45** and **46**).
4. **65** Protoxide of Manganese from the Alkalies. Mix the neutral or slightly acid solution with chloride of ammonium and precipitate the manganese with a slight excess of carbonate of ammonia. Allow the precipitate to settle in a warm place, filter through a thick filter, wash with hot water and weigh as protosesquioxide (H. Tamm[||]). In the filtrate separate the alkalies from the ammonia salts by gentle ignition. The separation of manganese as hydrated per-

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[*] Zeitschr. f. anal. Chem. 11, 424. [†] Ib. 12, 73.

[‡] Manganese may be separated from the alkalies according to § 109, 2, *b*. Nickel and cobalt may be separated from the alkalies according to **66**, substituting acetate of ammonia for acetate of soda.

[§] Zeitschr. f. anal. Chem. 9, 100. [||] Ib. 11, 425.

oxide cannot be recommended as the precipitate retains alkali.*

II. Separation of the Oxides of the Fourth Group from the Alkaline Earths.

§ 159.

Index :—The Nos. refer to those in the margin.
Oxide of zinc from baryta and strontia, 66, 67, 68, 73.
" lime, 66, 68, 73.
" magnesia, 66, 68.
Protoxide of manganese from baryta and strontia, 66, 67, 70, 71, 72.
" " lime and magnesia, 66, 70, 71, 72.
Protoxides of nickel and cobalt from baryta and strontia, 66, 67, 73, 75.
" " lime, 66, 73, 75.
" " magnesia, 66, 74.
Sesquioxide of iron from baryta and strontia, 66, 67, 69.
" " lime and magnesia, 66, 69.

A. *General Method.*

All Oxides of the Fourth Group from the Alkaline Earths.

66 Add chloride of ammonium, and, if acid, also ammonia, and precipitate with sulphide of ammonium, as in **63**. Take care to use slightly yellow sulphide of ammonium, perfectly saturated with sulphuretted hydrogen, and free from carbonate and sulphate of ammonia, and to employ it in sufficient excess. Insert the cork, and let the flask stand for some time to allow the precipitate to subside, then wash quickly, and as far as practicable, out of the contact of air, with water to which some sulphide of ammonium has been added. Acidify the filtrate with hydrochloric acid, heat, filter from the sulphur, and separate the alkaline earths, as directed § 154. If the filtrate is brownish from a little dissolved sulphide of nickel, acidify it with acetic acid instead of with hydrochloric acid, add some alkaline acetate, pass sulphuretted hydrogen, boil, and filter.

If the quantity of the alkaline earths is rather considerable, it is advisable to treat the slightly washed precipitate once more with hydrochloric acid (in presence of nickel or cobalt, it is not necessary to effect complete solution), heat the solution gently for some time, and then reprecipitate in the same way. If we have merely to effect the removal of nickel and cobalt, we may also, after addition of sulphide of ammonium, acidify with acetic acid, add acetate of soda, warm, pass sulphuretted hydrogen and filter; but it is always necessary to test the filtrate with sulphide of ammonium for nickel and cobalt. (Compare **90**.)

In separating manganese you may also use the method given § 109, 2, *b*, but in this case, too, a double precipitation is to be recommended.

B. *Special Methods.*

67 1. Baryta, Strontia, and Lime, from the whole of the Oxides of the Fourth Group.

Precipitate the baryta and strontia from the slightly acid solution with sulphuric acid (§§ 101, 102). The sulphate of baryta should first be washed with water acidified with hydrochloric acid, but even then you cannot be sure of getting it free from iron. The alkaline earthy sulphates after weighing must therefore always be tested for iron, &c.

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* Zeitschr. f. anal. Chem. 11, 298.

2. OXIDE OF ZINC FROM THE ALKALINE EARTHS. **68**

a. Convert the bases into acetates and precipitate the zinc from the solution according to § 108, 1, *b.*

b. Evaporate the solution of the chlorides with excess of chloride of ammonium, ignite the residue, and if necessary repeat the operation. The zinc is expelled as chloride, the alkaline earths remain behind.

3. SESQUIOXIDE OF IRON FROM THE ALKALINE EARTHS. **69**

a. Mix the somewhat acid solution with enough chloride of ammonium, boil, add slight excess of ammonia, boil till the excess of the latter is nearly expelled, and filter. The solution is free from iron, the precipitate is free from lime, baryta, and strontia, but contains a very slight trace of magnesia (H. ROSE[*]). In delicate analyses, after moderately washing the hydrated oxide of iron, redissolve it in hydrochloric acid, and repeat the precipitation.

b. Precipitate the sesquioxide of iron as basic acetate or formiate, compare **84** and **85**. The method is good, and can frequently be employed.

c. Precipitate the sesquioxide of iron with succinate of ammonia (**86**).

d. Decompose the nitrates by heat (**46**). A good method.[†]

e. Precipitate the dilute slightly acid solution with carbonate of baryta, and filter, after short digestion in the cold (**54**). Only applicable in the separation of sesquioxide of iron from lime and magnesia.

4. PROTOXIDE OF MANGANESE FROM THE ALKALINE EARTHS.

a. Methods based upon the separation of Manganese as Sesquioxide or Binoxide.

α. The methods (described in the last edition) of GIBBS,[‡] SCHIEL,[§] **70** H. ROSE,[||] and others, in which the manganese is thrown down as hydrated peroxide by peroxide of lead, by adding acetate of soda and passing chlorine, or by bromine, cannot be relied on, since decided traces of the alkaline earths are always coprecipitated with the manganese. Compare also R. FINKENER[¶], whose experience is the same. According to GIBBS[**] the error may be decreased by double precipitation. But as the precipitate usually contains alkali,[††] and is therefore unfit to weigh after simple ignition, these methods are rarely worth using.

β. DEVILLE's Method.[‡‡]—The bases must be present as nitrates. **71**

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[*] Pogg. Annal. 100, 300.

[†] Compare LATSCHINOW, Zeitschr. f. anal. Chem. 7, 213.

[‡] Annal. d. Chem. u. Pharm. 86, 54.

[§] Sillim. Journ. 15, 275.

[||] Pogg. Annal. 110, 305.

[¶] Handbuch d. anal. Chem. v. H. ROSE, 6 Aufl. v. FINKENER, 2, 925.

[**] Zeitschr. f. anal. Chem. 3, 331.

[††] *Ib.* 11, 298.

[‡‡] Journ. f. prakt. Chem. 60, 11.

Heat in a covered platinum dish to from 200° to 250°, until the formation of fumes has completely ceased, and the mass has become black; and proceed in all other respects as directed in **46**. The presence of a small quantity of organic matter, or the action of a too intense heat, may cause the reduction of traces of binoxide of manganese, and their solution in nitrate of ammonia; hence the solution must always be tested for manganese. The precipitate is, I find, never perfectly free from alkaline earths.

b. Methods based upon the Volumetric determination of Manganese, according to BUNSEN and KRIEGER.*

a. MANGANESE FROM MAGNESIA. **72**

Precipitate with solution of soda (§ 109, 1, *b*). Wash the precipitate thoroughly, ignite, and weigh. If the quantity of magnesia present is sufficient, the residue has the formula,

$$Mn_2O_3,MgO + xMgO.$$

Treat a weighed sample of it as directed in § 142; this will give the quantity of the manganese (1 eq. chlorine, or liberated iodine, corresponds to 1 eq. Mn_2O_3), and, by difference, the quantity of the magnesia.

β. FROM BARYTA AND STRONTIA.

Precipitate with carbonate of soda (§ 109, 1, *a*). The ignited precipitate has the formula,

$$Mn_2O_3,BaO + xBaO,CO_2.$$

Treat a sample as in *a*; this will give the quantity of the manganese. To find that of the carbonate of baryta, deduct the weight of the sesquioxide of manganese from that of the weighed precipitate, and add to the difference as much carbonic acid as has been expelled by the sesquioxide of manganese, that is, for each eq. Mn_2O_3, 1 eq. CO_2.

γ. FROM LIME.

Proceed as in *β*; but after ignition, moisten repeatedly with carbonate of ammonia, dry, and ignite gently, until the weight remains constant. Here, however, it is better to ignite the precipitate over the blast gas-lamp until the lime has become caustic.

N.B.—This method of volumetric determination of manganese presupposes the presence of more than 1 eq. MgO, CaO, &c., to 1 eq. Mn_2O_3; for if the case is different, the residue contains, besides Mn_2O_3, also Mn_2O_3,MnO. To adapt the method also to cases of the latter description, KRIEGER recommends the following process: dissolve a sample of the weighed precipitate, add half the weight of oxide of zinc, precipitate with carbonate of soda, ignite the precipitate some time in the air, weigh the product, and use it or an aliquot part of it, for the volumetric determination. It contains the whole of the manganese as Mn_2O_3. As will be seen, this modification greatly complicates the method. In precipitating manganese with soda or carbonate of soda remember the precautions given in § 109, 1, *a* and *b*, and that the precipitate must be exhausted with boiling water after ignition to free it from alkali.

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* Annal. d. Chem. u. Pharm. 87, 268.   † *Ib.* 43, 140.

5. PROTOXIDE OF COBALT, PROTOXIDE OF NICKEL, AND OXIDE OF ZINC, FROM BARYTA, STRONTIA, AND LIME.

Mix with carbonate of soda in excess, add cyanide of potassium, 73 heat very gently, until the precipitated carbonates of cobalt, nickel, and zinc are redissolved; then filter the alkaline earthy carbonates from the solution of the cyanides in cyanide of potassium. The former are dissolved in dilute hydrochloric acid, and separated according to § 154; the latter are separated according to § 160 (HAIDLEN and FRESENIUS*).

6. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM MAGNESIA.

Precipitate with a mixture of solution of hypochlorite of potassa 74 and solution of caustic potassa. The precipitate consists of sesquioxide of nickel, sesquioxide of cobalt, and hydrate of magnesia; wash thoroughly, and digest, whilst still moist, at a temperature of from 30° to 40°, with an excess of solution of chloride of mercury. In this process a double salt is formed of $MgCl + 3HgCl$, and the magnesia is dissolved, whilst a corresponding quantity of basic chloride of mercury precipitates (ULLGREN†). Evaporate the solution and washings, with addition of pure oxide of mercury, and determine the magnesia as directed § 104, 3, *b*. Remove the mercury from the oxides of nickel and cobalt by ignition, and separate the two metals as directed below.

7. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM BARYTA, STRONTIA, AND LIME.

Ignite the chlorides of the metals in hydrogen gas, and separate 75 the reduced nickel and cobalt from the chloride of barium, &c., by treating with water.

III. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM THOSE OF THE THIRD, AND FROM EACH OTHER.

§ 160.

Index :—The Nos. refer to those in the margin.

Alumina from oxide of zinc, 76, 77, 85, 86, 87, 97.
,, protoxide of manganese, 76, 77, 78, 85, 86, 108.
,, protoxides of nickel and cobalt, 76, 77, 80, 85, 86, 97.
,, protoxide of iron, 76, 77, 78, 85.
,, sesquioxide of iron, 77, 78, 84, 91, 92, 104.
Sesquioxide of chromium from oxide of zinc, protoxides of manganese, nickel, cobalt and iron, 76, 77, 93, 94.
,, sesquioxide of iron, 77, 91, 93, 94.
Oxide of zinc from alumina, 76, 77, 85, 86, 87, 97.
,, sesquioxide of chromium, 76, 77, 93, 94.
,, protoxide of manganese, 81, 87, 88, 109.
,, protoxide of nickel, 88, 100, 101, 102.
,, protoxide of cobalt, 88, 96, 99, 101, 102.
,, sesquioxide of iron, 76, 82, 85, 86, 103, 106.
Protoxide of manganese from alumina, 76, 77, 78, 85, 86, 108.
,, sesquioxide of chromium, 76, 77, 93, 94.
,, oxide of zinc, 81, 87, 88, 109.
,, protoxide of nickel, 81, 89, 90, 101.
,, protoxide of cobalt, 89, 90, 96, 101.
,, sesquioxide of iron, 76, 82, 85, 86, 108.

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[*] Annal. d. Chem. u. Pharm. 43, 140.

[†] BERZELIUS' Jahresber. 21, 146.

Protoxide of nickel from alumina, 76, 77, 80, 85, 86, 97.
,, sesquioxide of chromium, 76, 77, 93, 94.
,, oxide of zinc, 88, 100, 101, 102.
,, protoxide of manganese, 81, 89, 90, 101.
,, protoxide of cobalt, 95, 96, 98, 110.
,, sesquioxide of iron, 76, 80, 82, 85, 86, 89, 106.
Protoxide of cobalt from alumina, 76, 77, 80, 85, 86, 97.
,, sesquioxide of chromium, 76, 77, 93, 94.
,, oxide of zinc, 88, 96, 99, 101, 102.
,, protoxide of manganese, 89, 90, 96, 101.
,, protoxide of nickel, 95, 96, 98, 110.
,, sesquioxide of iron, 76, 80, 82, 85, 86, 89, 106.
Protoxide of iron from alumina, 76, 77, 78, 85.
,, sesquioxide of chromium, 76, 77, 93, 94.
,, sesquioxide of iron, 76, 83, 85, 105, 107, 111.
Sesquioxide of iron from alumina, 77, 78, 84, 91, 92, 104.
,, sesquioxide of chromium, 77, 91, 93, 94.
,, oxide of zinc, 76, 82, 85, 86, 103, 106.
,, protoxide of manganese, 76, 82, 85, 86, 108.
,, protoxide of nickel, 76, 80, 82, 85, 86, 89, 106.
,, protoxide of cobalt, 76, 80, 82, 85, 86, 89, 106.
,, protoxide of iron, 76, 83, 85, 105, 107, 111.

A. *General Methods.*

1. *Method based upon the Precipitation of some Oxides by Carbonate of Baryta.*

SESQUIOXIDE OF IRON, ALUMINA, AND SESQUIOXIDE OF CHROMIUM, FROM ALL OTHER BASES OF THE FOURTH GROUP.

76 Mix the sufficiently dilute solution of the chlorides or nitrates, but not sulphates, which must contain a little free acid,[*] in a flask, with a moderate excess of carbonate of baryta diffused in water; cork, and allow to stand some time in the cold, with occasional shaking. The sesquioxide of iron, alumina, and sesquioxide of chromium, are completely separated,[†] whilst the other bases remain in solution, with the exception perhaps of traces of protoxide of cobalt and protoxide of nickel, which will generally fall down with the precipitated oxides. This may be prevented, at least as regards nickel, by addition of chloride of ammonium to the fluid to be precipitated (SCHWARZENBERG[‡]). Decant, stir up with cold water, allow to deposit, decant again, filter, and wash with cold water. The precipitate contains, besides the precipitated oxides, carbonate of baryta; and the filtrate, besides the non-precipitated oxides, a salt of baryta.

If protoxide of iron is present, and it is wished to separate it by this method from sesquioxide of iron, &c., the air must be excluded during the whole of the operation. *a* is a flask in which the substance is dissolved, and the operations of precipitation and washing by decantation are effected. Carbonic acid enters through *b*, and in making the CO_2 apparatus it must be remembered that we have to depend on the pressure of the gas for filling *d*. The water in the bottle on the shelf to be used for washing should have been boiled and cooled in a current of carbonic acid. The glass tubes fitting in *a* should be smeared with tallow. In washing, the supernatant fluid, as clear as possible, is made to pass through the asbestos filter

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[*] If there is much free acid, the greater part of it must first be saturated with carbonate of soda.

[†] The separation of the sesquioxide of chromium requires the most time.

[‡] Annal. d. Chem. u. Pharm. 97, 216.

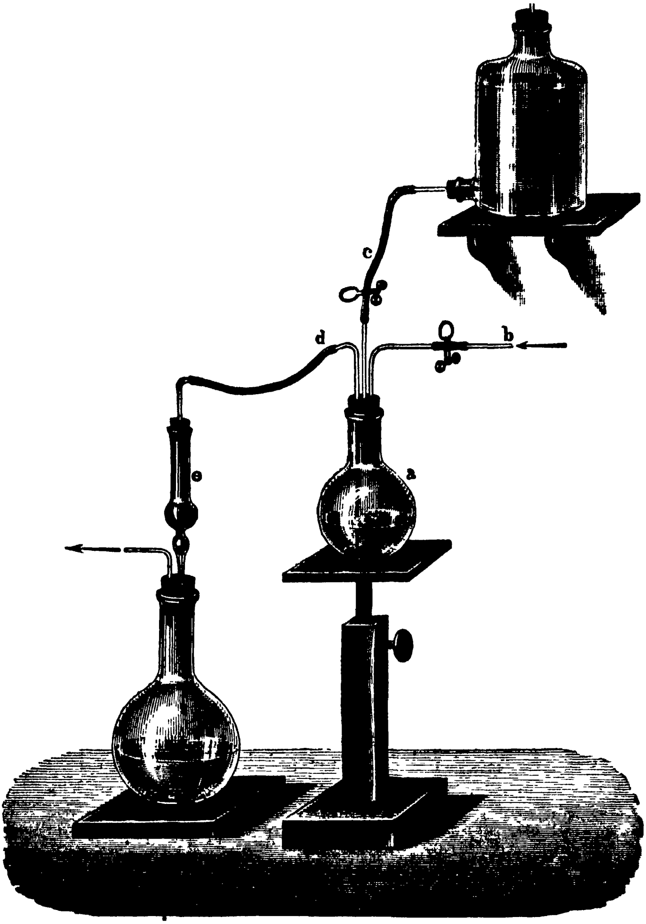

Fig. 104.

e. If *e* is placed sufficiently below *a*, *d*, when once filled, will act as a syphon.

2. *Method based upon the precipitation of the Oxides of the Fourth Group by Sulphide of Sodium, or Sulphide of Ammonium, from Alkaline Solution effected with the aid of Tartaric Acid.*

ALUMINA AND SESQUIOXIDE OF CHROMIUM FROM THE OXIDES OF THE FOURTH GROUP.

Mix the solution with pure neutral tartrate of potash,* then with 77 pure solution of soda or potassa until the fluid has cleared again;* add sulphide of sodium as long as a precipitate forms, allow it to deposit until the supernatant fluid no longer exhibits a greenish or brownish tint; decant, stir the precipitate up with water containing sulphide of sodium, decant again, transfer the precipitate, which contains all the metals of the fourth group, to a filter, wash with water containing sulphide of sodium, and separate the metals as directed in B. Add to the filtrate nitrate of potassa, and evaporate to dryness; fuse the residue in a platinum dish, and separate the alumina from the chromic acid formed as directed § 157. If you have merely to separate alumina from the oxides of the fourth group, it is better, after addition of tartrate of potash, to supersaturate with ammonia, add chloride of ammonium, and precipitate in a flask with sulphide of ammonium. When the precipitate has settled it is filtered off and washed with water containing sulphide of ammonium. The filtrate is evaporated in a platinum dish with carbonate of soda and nitrate of potassa to dryness, fused, and the alumina determined in the residue.

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* Tartaric acid often contains alumina, therefore this is best made from the bitartrate.

B. *Special Methods.*

1. *Methods based upon the Solubility of Alumina in Caustic Alkalies.*

a. Alumina from Protoxide and Sesquioxide of Iron, and Small Quantities of Protoxide of Manganese (but not from the protoxides of nickel and cobalt). 78

Mix the hydrochloric solution with carbonate of soda or pure potash till the greater part of the free acid is neutralized, and pour the solution gradually into excess of pure potash heated nearly to boiling in a platinum or silver dish, stirring all the while. Porcelain does not answer so well, and glass should on no account be used. The iron, if present as sesquichloride, separates as hydrated sesquioxide, while the alumina remains in solution as alkaline aluminate. The hydrated protosesquioxide of iron is more easy to wash than the sesquioxide, hence when much iron is present it is better to reduce a part by cautiously adding sulphite of soda and heating, so that when the solution is added to the boiling potash a black granular precipitate may be formed. The iron precipitate is sure to contain alkali, and must be dissolved in hydrochloric acid, the solution boiled with nitric acid if necessary, and reprecipitated with ammonia.

To the alkaline filtrate add a few drops of hydrochloric acid. If the potash was present in sufficient excess the precipitate will redissolve readily on stirring. Continue adding hydrochloric acid till in excess, boil with a little chlorate of potash (to destroy traces of organic matter), concentrate by evaporation, and throw down the alumina according to § 105, *a.* The above is the best method of procedure, but it is always to be feared that small quantities of alumina will be retained by the iron precipitate.

b. Alumina from Sesquioxide of Iron and Protoxides of Iron, Cobalt, and Nickel.

Fuse the oxides with hydrate of potassa in a silver crucible, boil 79 the mass with water, and filter the alkaline fluid, which contains the alumina, from the oxides, which are free from alumina, but contain potassa (H. Rose).

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* Sesquioxide of chromium and oxide of zinc cannot be obtained together in alkaline solution (Chancel, Compt. rend. 43, 927; Journ. f. prakt. Chem. 70, 378).

2. *Methods based on the different behavior of the Oxides to Ammonia or Carbonate of Ammonia in the presence of Chloride of Ammonium.*

a. Alumina and Sesquioxide of Iron from Protoxides of Cobalt and Nickel.

80 Sesquioxide of iron may be completely separated from these protoxides, by mixing the hot solution with chloride of ammonium, and then with excess of ammonia, digesting for several hours, washing the precipitate, redissolving in hydrochloric acid, reprecipitating with ammonia, and repeating the operation a third time. Nickel and cobalt are to be precipitated from the filtrate by addition of sulphide of ammonium, and subsequent neutralization with acetic acid.

If it is desired to remove the chloride of ammonium previously, this may be done by evaporating to dryness and heating the residue in a porcelain dish or crucible.[*]

In separating sesquioxide of iron and alumina from protoxides of nickel and cobalt, it is well to substitute carbonate of ammonia for ammonia, so as to insure the complete precipitation of the alumina.

b. Protoxide of Manganese from Protoxide of Nickel and Oxide of Zinc. 81

The solution should be slightly acid and contain chloride of ammonium. Precipitate the manganese as white carbonate with carbonate of ammonia, allow to settle in a warm place, filter through a thick paper, if necessary double, wash with hot water, dry the precipitate and convert it into protosesquioxide by ignition with access of air. This excellent method was proposed by Tamm,[†] and has given me good results.[‡] It is not adapted to the separation of cobalt from manganese, as the former is partly precipitated with the latter.

3. *Methods based upon the different deportment of neutralized Solutions at boiling heat.*

a. Sesquioxide of Iron from Protoxides of Manganese, Nickel and Cobalt, Oxide of Zinc, and other strong Bases, after Herschel,[§] Schwarzenberg[||] and my own Experiments. 82

Mix the dilute solution largely with chloride of ammonium (at least 20 of NH_4Cl to 1 of MnO, NiO, &c.), add carbonate of ammonia in small quantities, at last drop by drop and in very dilute solution, as long as the precipitated iron redissolves, which takes place promptly at first, but more slowly towards the end. As soon as the fluid has lost its transparency, without showing, however, the least trace of a distinct precipitate in it, and fails to recover its clearness after standing some time in the cold, but, on the contrary, becomes rather more turbid than otherwise, the reaction may be considered completed. When this point has been attained, heat slowly to boiling, and keep in ebullition for a short time after the carbonic acid has been entirely expelled. The sesquioxide of iron separates as a basic salt, which rapidly settles, if the solution was not too concentrated. Pour off the hot fluid through a filter and wash by decantation combined with filtration with boiling water containing a little chloride of ammonium. It is well to redissolve the precipitate in hydrochloric acid, and throw down the iron with ammonia. The first filtrate should be mixed with excess of ammonia. If a small portion of hydrated sesquioxide of iron is thrown down here, filter it off, dissolve in hydrochloric acid, precipitate with ammonia and thus free the small quantity of iron entirely from the strong bases; if, on the other hand, a larger quantity of iron is thrown down, this is a sign that the operation has been conducted improperly, and the hydrochloric solution of the precipitate must be reprecipitated as above. The fluid should not contain more than 3 or 4 grm. sesquioxide of iron in the litre, and should be tolerably free from sulphuric acid, as when this is present it is impossible to hit the exact point of saturation.

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[*] Platinum vessels may not be used, as they become spotted with nickel-platinum and are difficult to clean. This method, which I recommended in the last edition in the presence of small quantities of iron, has been found by v. Baumhauer (Zeitschr. f. anal. Chem. 10, 218), to be very suitable in the presence of large quantities.

[†] Chem. News, 26, 37. [‡] Zeitschr. f. anal. Chem. 11, 425.

[§] Annal. de Chim. et de Phys. 49, 306. [||] Annal. d. Chem. u. Pharm. 97, 216.

b. SESQUIOXIDE OF IRON FROM THE PROTOXIDE.

In compounds which dissolve with difficulty in hydrochloric acid, **83** but are decomposed by moderately concentrated sulphuric acid at a temperature below 326°,* SCHEERER† separates sesquioxide from protoxide of iron by dissolving in an atmosphere of carbonic acid (which is to be kept up during the entire experiment), diluting with pieces of ice free from air, adding carbonate of ammonia until the acid is nearly neutralized, then finely powdered magnesite (but not the artificial carbonate), and boiling from 10 to 15 minutes. The whole of the sesquioxide if iron is precipitated by this process. The precipitate is washed as in **76**, with water which, after being mixed with some sulphate of ammonia, has been boiled free from air and allowed to cool out of contact of air. v. KOBELL‡ prefers, as dissolving agent, a mixture of 1 vol. concentrated sulphuric acid, 2 vols. water, and 1 vol. strong hydrochloric acid. The solution may generally be effected with ease, without any oxidation of the protoxide of iron, by heating with hydrochloric acid or a mixture of 4 parts concentrated sulphuric acid and 1 part water in sealed tubes, at 210° (MITSCHERLICH§). Silicates are also very conveniently dissolved with hydrofluoric and hydrochloric acids, or hydrofluoric and dilute sulphuric acids. The silicate and its solvent being in a platinum dish on a water-bath, in order to prevent access of air place on the bath a cylinder of plaster of Paris with a cover. The cylinder may be readily made in the laboratory. It should have a hole bored in its side, through which carbonic acid should be passed during the operation, care being taken to fill the cylinder with the gas before commencing. Similar methods and apparatus have been described by WERTHER,[*] J. P. COOKE,[†] and WILBUR and WHITTLESEY.[‡] The hydrofluoric acid should be free from sulphuric and sulphurous acids.

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* Upon boiling, protoxide of iron is oxidized, the sulphuric acid being reduced to sulphurous acid (v. KOBELL, Annal. d. Chem. u. Pharm. 90, 244).

† Pogg. Annal. 86, 91, and 93, 448.

‡ Annal. d. Chem. u. Pharm. 90, 244.

§ Zeitschr. f. anal. Chem. 1, 54.

c. SESQUIOXIDE OF IRON FROM ALUMINA. 84

The metals may be present as chlorides or sulphates. Mix the dilute solution if necessary with carbonate of soda to neutralize any large excess of free acid, then add hyposulphite of soda till all the sesquisalt of iron is reduced to protosalt, now add more hyposulphite and boil for some time till all odor of sulphurous acid has entirely disappeared. The alumina is precipitated in accordance with the following reaction: $Al_2O_3,3SO_3 + 3(NaO,S_2O_2) + 3HO = Al_2O_3,3HO + 3(NaO,SO_3) + 3SO_2 + S_3$. Filter, wash the precipitate well and ignite. Decompose the excess of hyposulphite of soda in the filtrate by heating with hydrochloric acid, filter off the separated sulphur, and determine the iron (CHANCEL[§]).

4. *Method based on the behavior of the Acetates at a boiling heat.*

SESQUIOXIDE OF IRON AND ALUMINA FROM PROTOXIDE OF MANGANESE, OXIDE OF ZINC AND PROTOXIDES OF COBALT, NICKEL, AND IRON. 85

The metals should be present in the form of chlorides. The solution should be in a flask. If much free acid is present first nearly neutralize with carbonate of soda or of ammonia; the solution should remain clear, but if there is much sesquichloride of iron it should be of a deep red color. Add a concentrated solution of neutral acetate of soda or of ammonia, not in large excess, and boil for a short time—long continued boiling would make the precipitate slimy. When the lamp is removed the precipitate should settle rapidly, leaving the supernatant fluid clear. Wash the precipitate immediately by decantation and filtration with boiling water containing a little acetate of soda or ammonia. In very particular analyses it would be well after washing the precipitate a little to redissolve it in hydrochloric acid and reprecipitate.

In separating sesquioxide of iron from the protoxide REICHARDT[‖] recommends a slight addition of chloride of ammonium or of sodium to prevent oxidation of the protoxide.

The precipitate of basic acetate of sesquioxide of iron or basic acetate of alumina is best dissolved in hydrochloric acid, in order to precipitate the bases from this solution again by ammonia. This method is more suitable to the separation of sesquioxide of iron or of sesquioxide of iron and alumina from the strong bases than to the separation of alumina alone. It is a good method, and is very generally used.

Instead of the alkaline acetates, the corresponding formates may be employed with the best result (§ 81,*f*).

[*] Journ. f. prakt. Chem. 91, 329.

[†] Zeitschr. f. anal. Chem. 7, 99.

[‡] *Ib.* 10, 98.

[§] Compt. rend. 46, 987. Compare also WERTHER, Journ. f prakt. Chem. 91, 329, and GIBBS, Zeitschr. f. anal. Chem. 3, 391. This method has been so frequently recommended, that I have thought it necessary to give it. I must add, however, I have not found it perfectly trustworthy.

[‖] Zeitschr. f. anal. Chem. 5, 64.

5. *Method based on the different behavior of the Succinates.*

SESQUIOXIDE OF IRON (AND ALUMINA) FROM OXIDE OF ZINC, AND PROTOXIDES OF MANGANESE, NICKEL, AND COBALT. 86

The solution should contain no considerable quantity of sulphuric acid. If acid, as is usually the case, add ammonia till the color is reddish-brown, then acetate of soda, or of ammonia (H. ROSE) till the color is deep red, finally precipitate with neutral alkaline succinate at a gentle heat, and when cool filter the succinate of sesquioxide of iron from the solution which contains the rest of the metals. Wash the precipitate first with cold water, then with warm ammonia, which removes the greater part of the acid, leaving it darker in color. Dry and ignite, moisten with a little nitric acid, and ignite again. With proper care the separation is complete, and especially to be recommended when a relatively large quantity of iron is present. The method may also be used in the presence of alumina. The latter falls down completely with the iron (E. MITSCHERLICH, PAGELS*).

6. *Methods based upon the different deportment of the several Sulphides with Acids, or of the Acetic Acid Solutions with Sulphuretted Hydrogen.*

a. OXIDE OF ZINC FROM ALUMINA AND PROTOXIDE OF MANGANESE.

87 The solution of the acetates, which must be free from inorganic acids, and must contain a sufficient excess of acetic acid, is precipitated with sulphuretted hydrogen, which throws down the zinc only (§ 108, *b*). The oxides are usually most readily obtained in acetic acid solution, by converting them into sulphates, and adding a sufficient quantity of acetate of baryta. Sulphuretted hydrogen is then conducted, without application of heat, into the unfiltered fluid, to which, if necessary, some more acetic acid has been added. The precipitate, which consists of a mixture of sulphide of zinc and sulphate of baryta, is washed with water containing sulphuretted hydrogen. It is then heated with dilute hydrochloric acid, the solution filtered, and the zinc in the filtrate determined as directed § 108, *a*. The other oxides are determined in the fluid filtered from the sulphide of zinc, after removal of the baryta by precipitation. BRUNNER† has proposed a modification of this process, especially for the separation of zinc from nickel.

b. OXIDE OF ZINC FROM PROTOXIDES OF NICKEL, COBALT, AND MANGANESE. 88

To the hydrochloric solution add carbonate of soda till a permanent precipitate just forms, and then a drop or two of hydrochloric acid to redissolve the precipitate. Now pass sulphuretted hydrogen till the precipitate of sulphide of zinc ceases to increase. Add a few drops of a very dilute solution of acetate of soda, and continue passing the gas for some time. When all the zinc is precipitated, allow to stand for 12 hours, filter, wash with sulphuretted hyrogen water, and estimate the nickel and cobalt in the filtrate (SMITH and BRUNNER†). A good method; compare KLAYE and

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* Jahresber. v. KOPP u. WILL. 1858, 617.

† Dingler's polyt. Journ. 150, 369; Chem. Centralbl. 1859, 26.

DEUS.* The method is also adapted for separating zinc from manganese.

89 *c.* PROTOXIDES OF COBALT AND NICKEL FROM PROTOXIDE OF MANGANESE AND THE OXIDES OF IRON.

The solution, which must be free from nitric acid, is, after neutralization of any free acid which may be present by ammonia, precipitated with sulphide of ammonium, highly dilute hydrochloric acid then added, and sulphuretted hydrogen gas conducted into the fluid to saturation, with frequent stirring. This serves to dissolve the sulphide of manganese and the sulphide of iron, whilst the sulphide of cobalt and the sulphide of nickel, though the latter less completely, remain undissolved. The filtrate is reprecipitated by addition of ammonia and sulphide of ammonium, and the above treatment is repeated. The results are accurate. It is important, however, to test the weighed cobalt and nickel compounds, for manganese and iron.

d. PROTOXIDES OF COBALT AND NICKEL FROM PROTOXIDE OF MANGANESE.

90 To the acid solution add carbonate of soda in excess, then acetic acid in good excess, then to the clear fluid, containing say 1 grm. of nickel or cobalt, 30 to 50 c.c. of acetate of soda solution (1 in 10), and pass sulphuretted hydrogen to saturation, keeping at 70°. Filter off the precipitated sulphide of nickel or cobalt, wash and dry it. Concentrate the filtrate by evaporation, add sulphide of hydrogen and ammonium, and then excess of acetic acid, thus obtaining a second slight precipitation of nickel or cobalt. Test the filtrate again in the same manner. In the mixed precipitates estimate nickel or cobalt according to § 110, 1, *b*, *a*, or § 111, 1, *c*; in the filtrate the manganese according to § 109, 2.

7. *Methods based upon the different deportment of the several Oxides with Hydrogen Gas at a red heat.*

a. SESQUIOXIDE OF IRON FROM ALUMINA AND SESQUIOXIDE OF CHROMIUM.

91 RIVOT'S Method.†—Precipitate with ammonia, heat, filter, ignite and weigh. Triturate, and weigh off a portion in a porcelain boat. Insert the latter into a porcelain tube, supported in a horizontal position, through which a stream of hydrogen (dried with sulphuric acid and chloride of calcium) is passing. In the open end of the porcelain tube is inserted a perforated cork, with a narrow open glass tube. When the air is expelled from the apparatus, heat the porcelain tube gradually to redness, and maintain it at that temperature as long as water forms (about 1 hour). Allow the tube now to cool, still maintaining the current of hydrogen, then remove the boat, and weigh it. The loss of weight indicates the quantity of oxygen which was combined with the iron to sesquioxide.

If you wish to determine the oxides separately, which may be deemed more particularly necessary if the substance contains little sesquioxide of iron, treat the mixture of alumina, sesquioxide of chromium, and metallic iron, with highly dilute nitric acid (1 part of acid to 30 or 40 parts of water), or with water to which very little nitric acid is added from time to time. The iron is dissolved, the alumina and sesquioxide of chromium remain undissolved. The latter oxides are weighed; the iron is precipitated by ammonia, after ebullition of the fluid. The results of RIVOT's experimental analyses were highly satisfactory. The method is more particularly suitable in cases where the quantity of alumina, &c., is large and that of iron small.

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* Zeitschr. f. anal. Chem. 10, 200.

† Annal. de Chim. et de Phys. 30, 188; Journ. f. prakt. Chem. 51, 338.

b. SESQUIOXIDE OF IRON FROM ALUMINA.

DEVILLE transmits through the tube, after the reduction by hydrogen has been effected as in *a*, first hydrochloric gas, and then again hydrogen. This leaves the alumina in a state of purity; the iron volatilizes as protochloride, and is either determined by the loss or in the direct way. If the latter mode is adopted, the protochloride in the tubes and in the tubulated receiver is dissolved by heating dilute hydrochloric acid to boiling, and conducting the vapor into the porcelain tube; the tubulure of the receiver is directed downwards in this operation. The operation is much facilitated by the use of a platinum tube (COOKE*). 92

8. *Methods based upon the different capacity of the several Oxides to be converted by Oxidizing Agents into higher Oxides, or by Chlorine into higher Chlorides.*

a. SESQUIOXIDE OF CHROMIUM FROM ALL THE OXIDES OF THE FOURTH GROUP, AND FROM ALUMINA.

α. Fuse the oxides with nitrate of potassa and carbonate of soda (comp. 59), boil the mass with water, add a small quantity of spirit of wine, and heat gently for several hours. Filter and determine in the filtrate the chromium as directed § 130, and in the residue the bases of the fourth group. The following is the theory of this process: the oxides of zinc, cobalt, nickel, iron, and partly that of manganese, separate upon the fusion, whilst, on the other hand, manganate (perhaps also some ferrate) and chromate of potassa are formed. Upon boiling with water, part of the manganic acid of the manganate of potassa is converted into permanganic acid at the expense of the oxygen of another part, which is reduced to the state of binoxide; the latter separates, whilst the potassa salts are dissolved. The addition of alcohol, with the application of a gentle heat, effects the decomposition of the manganate and permanganate of potassa, binoxide of manganese being separated. Upon filtering the mixture, we have therefore now the whole of the chromium in the filtrate as alkaline chromate, and all the oxides of the fourth group on the filter. Alumina, if present, will be found partly in the residue, partly as alkaline aluminate in the filtrate; proceed with the latter according to 59. 93

If you have to deal with the native compound of sesquioxide of chromium with protoxide of iron (chromic iron) the above method does not answer. The method of analysing this substance will be given in the *Special Part.*

β. Nearly neutralize the solution, add acetate of soda, heat and convert the sesquioxide of chromium into chromic acid by passing 94 chlorine, compare 61. If sesquioxide of iron and alumina are present, they will separate during boiling by the action of the acetate of soda, while the chromic acid and any oxide of zinc will remain in solution. If manganese, nickel and cobalt are present, the method loses its simplicity; the manganese is precipitated as hydrated peroxide with a portion of the cobalt, almost the whole of the nickel and some zinc, while the chromic acid remains in solution with the principal amount of the zinc and the rest of the cobalt and nickel (W. GIBBS).

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* Zeitschr. f. anal. Chem. 6, 226.

b. PROTOXIDE OF COBALT FROM PROTOXIDE OF NICKEL.

α. After H. ROSE.* Dilute the hydrochloric acid solution, in a capacious flask, with water (1 litre to 2 grm. of oxides) conduct chlorine gas into the flask until the fluid is saturated, and the vacant space in the flask completely filled with the gas; add excess of carbonate of lime or baryta shaken up with water, let the mixture stand 5 or 6 hours in the cold, taking care to shake repeatedly; then filter the fluid which contains the whole of the nickel, from the precipitated sesquioxide of cobalt. HENRY has substituted bromine for chlorine with success. DENHAM SMITH recommends addition of a dilute solution of chloride of lime which has been completely decomposed with sulphuric acid, so as to leave no hypochlorite in it. 95

FR. GAUHE† has found the method unsafe, as a short action of the alkaline earthy carbonates scarcely precipitates the cobalt, while a long action throws down nickel with it. The method may therefore be of service under special conditions and when applied with experience, but is unsuitable for accurate analysis.

β. The method of GIBBS, elaborated by H. ROSE‡, which consists in boiling the sulphuric acid solution with binoxide of lead, yields also only approximate results, compare GAUHE (*loc. cit.*)

9. *Method based upon the different deportment of the Nitrites.*

PROTOXIDE OF COBALT FROM PROTOXIDE OF NICKEL, ALSO FROM PROTOXIDE OF MANGANESE AND OXIDE OF ZINC.

The separation of cobalt as nitrite of sesquioxide of cobalt and potassa, was recommended first by FISCHER,§ afterwards by A. STROMEYER,‖ GENTH and GIBBS,¶ H. ROSE,** FR. GAUHE†† and myself (compare last edition of this work). The results are quite satisfactory both in presence of much cobalt and little nickel, and in the presence of little cobalt and much nickel; but the process is peculiarly good for the latter case. However, it is absolutely necessary that baryta, lime, and strontia should be absent, as in their presence nickel is thrown down as triple nitrite of protoxide of nickel, potassa, and alkaline earth (KÜNZEL, O. L. ERDMANN‡‡). The best way of proceeding is as follows:—The solution of the oxides (from which any iron must first be separated) is evaporated to a small bulk, and then, if much free acid is present, neutralized with potassa. Then add a concentrated solution of nitrite of potassa (previously neutralized 96 with acetic acid and filtered from any flocks of silica and alumina that may have separated) in sufficient quantity, and finally acetic acid, till any flocculent precipitate that may have formed from excess of potassa, has redissolved and the fluid is decidedly acid. Allow it to stand at least for 24 hours in a warm place, take out a portion of the supernatant fluid with a pipette, mix it with more nitrite of potassa, and observe whether a further precipitation takes place in this after long standing. If no precipitate is formed the whole of the cobalt has fallen down, *otherwise the small portion must be returned to the principal solution, some more nitrite of* potassa added, and after long standing the same test applied. Thus, and thus alone, can the analyst be sure of the complete precipitation of the cobalt. Finally filter and treat the precipitate according to § 111, 1, *d*. Boil the filtrate with excess of hydrochloric acid, precipitate with potash, redissolve the precipitate in hydrochloric acid, throw down the nickel according to p. 209, γ, as sulphide, and then convert into protoxide or metal. In this manner alone can the nickel be obtained pure, as the original filtrate contains so much alkaline salt and also generally alumina and silica.

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* Pogg. Annal. 71, 545, and Handb. der anal. Chem. 6 Aufl. II. 143.

† Zeitschr. f. anal. Chem. 5, 84.

‡ Pogg. Annal. 110, 413.

§ *Ib.* 72, 477.

‖ Annal. d. Chem. u. Pharm. 96, 218.

¶ *Ib.* 104, 309.

** Pogg. Annal. 110, 412.

†† Zeitschr. f. anal. Chem. 5, 74.

‡‡ Zeitschr. f. anal. Chem. 3, 161; Journ. f. prakt. Chem. 97, 387.

10. *Methods based upon the different deportment with Cyanide of Potassium.*

a. ALUMINA FROM OXIDE OF ZINC, PROTOXIDE OF COBALT, AND PROTOXIDE OF NICKEL.

Mix the solution with carbonate of soda, add cyanide of potassium in sufficient quantity, and digest in the cold, until the precipitated carbonates of zinc, cobalt and nickel are redissolved. Filter off the undissolved alumina, wash, and remove the alkali which it contains, by resolution in hydrochloric acid and reprecipitation by ammonia (FRESENIUS and HAIDLEN[*]). 97

b. PROTOXIDE OF COBALT FROM PROTOXIDE OF NICKEL.

LIEBIG's method,[†] which depends upon the conversion of the cobalt into cobalticyanide of potassium, and of the nickel into double cyanide of nickel and potassium, has been carefully studied in my laboratory by FR. GAUHE.[‡] It has been thus found that boiling the solution containing cyanide of potassium and hydrocyanic acid (LIEBIG's first method) does not completely convert the double cyanide of cobalt and potassium first formed into cobalticyanide of potassium, but that passing chlorine (LIEBIG's second method) effects a ready and thorough conversion. The method then gives a very excellent separation, and is more particularly to be recommended where the quantity of nickel is small in proportion to the cobalt. We proceed as follows, taking a hydrochloric solution of the metals. Remove the greater part of the free acid by evaporation or neutralize it by potash, add pure cyanide of potassium till the precipitate first formed has redissolved, then add more cyanide, dilute, boil for some time or not, as you like, pass chlorine through the cold fluid, adding potash or soda occasionally, so that the fluid may remain strongly alkaline to the end. Bromine may be used instead of chlorine, and indeed is far more convenient. In the course of an hour 98 the whole of the nickel will have precipitated as black hydrate of the sesquioxide. Having taken out a portion and satisfied yourself of this by addition of a further quantity of chlorine or bromine, filter and wash with boiling water. The precipitate always retains alkali, and must be redissolved in hydrochloric acid, and estimated according to § 110, 1, *a*, or 2.

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[*] Annal. d. Chem. u. Pharm. 43, 129.

[†] *Ib.* 65, 244, and 87, 128.

[‡] Zeitschr. f. anal. Chem. 5, 75.

As regards the cobalt it is most convenient to estimate it by difference. But if you wish to make a direct estimation it will be advisable, in consequence of the large quantity of salts present in solution, first to evaporate to dryness with excess of hydrochloric acid, to take up the residue with a little water, and to heat in a large platinum dish, with the addition of excess of pure concentrated sulphuric acid till the greater part of the sulphuric acid has escaped. The red mass, consisting principally of alkaline bisulphate. is then treated with water, and the cobalt estimated according to § 111, 1, *c*.

Another method of separating nickel and cobalt by cyanide of potassium, has been described by FLECK;* but it does not have the appearance of being an improvement upon the foregoing. It depends upon the fact that although monosulphide of cobalt, like sulphide of nickel, dissolves readily in cyanide of potassium, the same is not the case with the sulphide of cobalt precipitated by sulphide of ammonium from a solution of cobalt, which has been mixed with ammonia in excess, and exposed to the action of the air till its color ceases to change.

c. PROTOXIDE OF COBALT FROM OXIDE OF ZINC.

Add to the solution of the two oxides, which must contain **99** some free hydrochloric acid, common cyanide of potassium (prepared by LIEBIG's method), in sufficient quantity to redissolve the precipitate of protocyanide of cobalt and cyanide of zinc which forms at first; then add a little more cyanide of potassium, and boil some time, adding occasionally one or two drops of hydrochloric acid, but not in sufficient quantity to make the solution acid. After cooling add some chlorine or bromine, and digest for some time to complete the conversion of the cobalt into cobalticyanide of potassium. Mix the solution with hydrochloric acid in an obliquely placed flask, and boil until the cobalticyanide of zinc which precipitates at first is redissolved, and the hydrocyanic acid completely expelled. Add solution of soda or potassa in excess, and boil until the fluid is clear; the solution may now be assumed to contain all the cobalt as cobalticyanide of potassium, and all the zinc as a compound of oxide of zinc and alkali. Precipitate the zinc by sulphuretted hydrogen (§ 108). Filter, and determine the cobalt in the filtrate as in **98**. The process is simple and the separation complete (FRESENIUS and HAIDLEN).

d. PROTOXIDE OF NICKEL FROM OXIDE OF ZINC.

Mix the concentrated solution of both oxides with an excess of **100** concentrated pure solution of potassa, then with hydrocyanic acid in sufficient quantity to redissolve the precipitate completely; add solution of monosulphide of *potassium*, allow the precipitated sulphide of zinc to deposit at a gentle heat, filter, wash the sulphide of zinc with dilute sulphide of potassium, treat the precipitate with hydrochloric acid, and precipitate the zinc from the solution with carbonate of soda according to § 108, 1, *a*. Determine the nickel in the filtrate by heating with fuming hydrochloric acid and nitric acid (or chlorate of potash), evaporating and precipitating with potash (WÖHLER*).

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* Journ. f. prakt. Chem. 97, 303; Zeitschr. f. anal. Chem. 5, 399.

KLAYE and DEUS,† who examined this method in my laboratory, found that pure and freshly dissolved cyanide of potassium might be used instead of potash and hydrocyanic acid. The presence of carbonate or formate of ammonia or cyanate of potash in the cyanide of potassium would interfere considerably with the complete precipitation of the zinc as sulphide. The sulphide of zinc may also be finally washed with water containing sulphuretted hydrogen, and determined according to § 108, 2.

c. COBALT AND NICKEL FROM MANGANESE AND ZINC (W. GIBBS‡).

To the solution of the chlorides add acetate of soda and pass hydrocyanic acid gas. Cyanide of zinc is immediately thrown down as a white powder more or less completely. Now add sulphide of sodium, which will convert the zinc and manganese into sulphides, whilst the cobalt and nickel will remain in solution as double cyanides, and may be separated according to **98**. The use of gaseous hydrocyanic acid is a great drawback to this method. **101**

11. *Methods based upon the Volatility of Zinc.*

a. PROTOXIDES OF COBALT AND NICKEL FROM OXIDE OF ZINC.

BERZELIUS§ recommends the following method for the absolute separation of cobalt and nickel from zinc :—Precipitate with solution of potassa, in excess, boil, and filter the fluid, which contains the greater portion of the zinc dissolved in the caustic potassa, from the precipitated hydrated protoxides of nickel and cobalt, which also contain some of the zinc ; wash the precipitate *thoroughly* with boiling water, and determine the zinc in the filtrate as directed § 108. Dry the precipitate, ignite, and weigh ; then mix in a porcelain crucible with pure sugar (recrystallized from alcohol), and heat slowly until the sugar is completely carbonized. Place the crucible, with the lid on, in a bath of magnesia in a larger-sized covered clay crucible, and expose for the space of 1 hour to the very highest degree of heat attainable by a wind furnace. This process causes the reduction of the metals : the whole of the zinc present rises in vapor, the nickel and cobalt, mixed with charcoal, remain. Treat the residue with nitric acid, and determine the oxides by precipitating with potassa, and weighing the precipitate. The difference between this weight and that obtained before, shows the quantity of the coprecipitated oxide of zinc. **102**

KLAYE and DEUS,‖ who tested this method in my laboratory, obtained a very good result. The sugar causes much intumescence, and they recommend the use of charcoal obtained from sugar instead. An attempt was made to employ the gas blowpipe instead of the furnace, but this was a failure.

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* Annal. d. Chem. u. Pharm. 89, 376.

† Zeitschr. f anal. Chem. 10, 197.

‡ *Ib.* 3, 332.

§ His Jahresbericht, 21, 144.

‖ Zeitschr. f. anal. Chem. 10, 192.

b. ZINC FROM IRON, IN ALLOYS.

BOBIERRE states that these alloys may be readily and accurately analysed by igniting them in a stream of hydrogen. **103**

12. *Methods based upon the Volumetric Determination of one of the Oxides, and the finding of the other from the difference.*

a. SESQUIOXIDE OF IRON FROM ALUMINA.

Precipitate both oxides with ammonia (§ 105, *a*, and § 113, 1). **104** Dissolve the weighed residue, or an aliquot part of it, by digestion with concentrated hydrochloric acid, or by fusion with bisulphate of potassa and treatment with water containing sulphuric acid; and determine the iron volumetrically as directed § 113, 3, *a*, or *b*. The alumina is found from the difference. This is an excellent method, and to be recommended more particularly in cases where the relative amount of iron is small. If you have enough substance it is of course much more convenient to divide the solution, by weighing or measuring, into 2 portions, and determine in the one the sesquioxide of iron + alumina, in the other the iron. Instead of titrating the iron, you may also precipitate it, after addition of tartaric acid and ammonia, with sulphide of ammonium (**77**).

b. SESQUIOXIDE OF IRON FROM PROTOXIDE OF IRON (OXIDE OF ZINC, PROTOXIDE OF NICKEL).

a. Determine in a portion of the substance the total amount of **105** the iron as sesquioxide, or by the volumetric way. Dissolve another portion by warming with sulphuric acid in a flask through which carbonic acid is conducted, to exclude the air; dilute the solution, and determine the protoxide of iron volumetrically (§ 112, 2, *a*). The difference gives the quantity of the sesquioxide. Or, dissolve the compound in like manner in hydrochloric acid, and determine the sesquichloride of iron with protochloride of tin according to § 113, 3, *b*. In this case the difference gives the protoxide of iron. If it is desired to determine the protochloride of iron in the hydrochloric solution directly, it will be well to use **PENNY'S** method (p. 220). These convenient and simple methods will in time probably replace the older and more complicated methods of determining protoxide of iron in presence of sesquioxide. If the compound in which sesqui- and protoxide of iron are to be estimated is decomposed by acids with difficulty, heat it with a mixture of 4 parts sulphuric acid and 1 part water (or with hydrochloric acid) in a sealed tube at 210° (**MITSCHERLICH**, compare p. 354). Or, if this is not enough, fuse it with borax (1 part mineral, 5—6 vitrified borax) in a small retort, connected with a flask containing nitrogen (produced by combustion of phosphorus in air); an atmosphere of carbonic acid is less suitable. Triturate the fused mass with the glass, and dissolve in boiling hydrochloric acid in an atmosphere of carbonic acid (**HERMANN V. KOBELL**). Or you may dissolve the substance in a mixture of hydrofluoric and hydrochloric acids as directed **83**—and this will generally be the best way.

Iron may also be determined volumetrically in presence of oxide 106
of zinc, protoxide of nickel, &c. It is, indeed, often the better way, instead of effecting the actual separation of the oxides, to determine in one portion of the solution the sesquioxide of iron + oxide of zinc or + protoxide of nickel, in another portion the iron alone, and to find the quantity of the other metal by the difference. However, this can be done only in cases where the quantity of iron is relatively small.

β. SESQUIOXIDE OF IRON FROM PROTOXIDE OF IRON. 107
BUNSEN's method. Fill the little flask *d*, fig. 85 (p. 292), two-thirds with fuming hydrochloric acid, and replace the air above with carbonic acid, by throwing some grains of carbonate of soda into the flask. Weigh a portion of the substance in an open short tube, and in another similar tube a slight excess of bichromate of potassa; drop the two tubes into the flask, attach the evolution tube, and proceed for the rest as directed § 130, *e*, *β*. Of course you will obtain less free iodine than if no protoxide of iron had been dissolved with the chromate of potassa, as a portion of the liberated chlorine goes to convert the protochloride of iron into sesquichloride. The difference between the iodine corresponding to the bichromate used and that actually obtained represents the protoxide of iron present (1 eq. iodine = 2 eq. protoxide of iron).

If you wish to ascertain the total quantity of iron present, dissolve another portion of the substance in hydrochloric acid in the little flask, and reduce the sesquioxide of iron to protoxide, by means of a ball of chemically pure zinc, cast on a fine platinum wire. To exclude all access of air, connect the flask, during the ebullition, with the apparatus *b b'* (fig. 105).

As soon as the colorless condition of the fluid shows that the reduction is completed, cool the flask in cold water, lift the upper cork, throw a few grains of carbonate of soda into the acid, draw the zinc ball up the tube *b*, wash off the fluid adhering to the ball into the flask, and remove *b b'*. Add quickly a weighed slight excess of bichromate of potassa, and proceed for the rest as just directed.

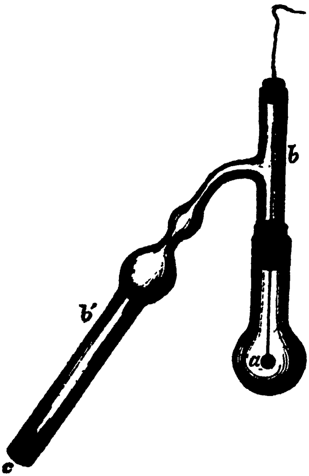

Fig. 105.

c. PROTOXIDE OF MANGANESE FROM ALUMINA AND SESQUIOXIDE OF IRON (KRIEGER*).

Precipitate with carbonate of soda, digest the precipitate some 108
time with the fluid, wash properly, first by decantation, then on the filter, dry, ignite, and determine in a sample the manganese according to 72. Bear in mind that the precipitate contains the manganese as Mn_3O_4, and also that in precise analyses the small

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* Annal. d. Chem. u. Pharm. 87, 261.

quantity of manganese in the filtrate must not be disregarded (§ 109, 1, *a*). Carbonate of ammonia may be used instead of carbonate of soda (**65**) and deserves the preference.

d. PROTOXIDE OF MANGANESE FROM OXIDE OF ZINC (KRIEGER).

Precipitate boiling with carbonate of soda, wash the precipitate **109** with boiling water, dry, and ignite. If the substance contained a sufficient quantity of zinc, the precipitate consists of $ZnO + xMn_2O_3$. Weigh off a portion and determine the manganese as in **72**. If the quantity of zinc is insufficient, proceed as directed **72**, *N.B.* Regarding the minute quantity of manganese which passes into the filtrate, see § 109, 1, *a*.

e. PROTOXIDE OF COBALT FROM PROTOXIDE OF NICKEL.

Estimate both metals according to § 110, 1, *a* and 2, and § 111, **110** 1, *b*, dissolve the reduced metals in aqua regia, evaporate repeatedly with hydrochloric acid to dryness, till the nitric acid is expelled, determine the cobalt according to § 111, 3, and find the nickel by difference. The method cannot be employed in presence of large quantities of nickel and only gives tolerably good results.

13. *Indirect Method.*

SESQUIOXIDE OF IRON FROM PROTOXIDE.

Of the many indirect methods proposed, which are now, however, **111** but rarely resorted to since the introduction of the volumetric methods, I will only give the following:—Dissolve in hydrochloric acid in a current of carbonic acid, add solution of sodio-terchloride of gold in excess, close the flask, and allow the reduced gold to deposit; filter the fluid from the gold, and determine the latter as directed § 123. Determine the total quantity of the iron in the filtrate, or in another portion of the substance. The calculation is self-evident: 1 eq. gold separated corresponds to 6 eq. protochloride or protoxide of iron, since $6FeCl + AuCl_3 = 3Fe_2Cl_3 + Au$ (H. ROSE).

IV. SEPARATION OF SESQUIOXIDE OF IRON, ALUMINA, PROTOXIDE OF MANGANESE, LIME, MAGNESIA, POTASSA, AND SODA.

§ 161.

As these oxides are found together in the analysis of most silicates, and also in many other cases, I devote a distinct paragraph to the description of the methods which are employed to effect their separation.

1. *Method based upon the employment of Carbonate of Baryta* (particularly applicable in cases where the mixture contains only a small proportion of lime).

The solution should contain no free chlorine, and the iron should **112** be all in the form of sesquioxide. Precipitate the iron and alumina by carbonate of baryta* (**54** and **76**), dissolve the precipitate in hydrochloric acid, throw down the baryta with sulphuric acid, filter, and estimate the iron and alumina according to one of the methods given § 160, by preference **104**, at least when the quantity of alumina is not too small.

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* Before adding the carbonate of baryta, it is *absolutely indispensable* to ascertain whether a solution of it in hydrochloric acid is completely precipitated by sulphuric acid, so that the filtrate leaves no residue upon evaporation in a platinum dish.

To the filtrate from the carbonate of baryta precipitate add hydrochloric acid, heat, throw down the baryta with sulphuric acid, added just in excess. Filter off the precipitate, wash till free from soluble sulphate, concentrate if necessary, precipitate, and estimate the manganese as sulphide (§ 109, 2). To the filtrate add hydrochloric acid, heat, filter off the sulphur, precipitate the lime with oxalate of ammonia, and finally separate the magnesia from the alkalies by one of the methods given § 153.

2. *Method based upon the application of Alkaline Acetates or Formates.*

Remove by evaporation any very considerable excess of acid which may be present, dilute, add carbonate of soda,* until the fluid is nearly neutral (no permanent precipitate must be formed), then acetate or formate of soda, and proceed according to **85**. Wash the precipitate well, dissolve in hydrochloric acid, precipitate the solution with ammonia (**45**), dry, ignite, and weigh. Dissolve in concentrated hydrochloric acid, and determine the iron volumetrically by means of protochloride of tin, &c., according to § 113, 3, *b*, or digest it with 16 times its weight of a mixture of 8 parts sulphuric acid and 3 parts water, or fuse it for a long time with bisulphate of potassa, dissolve in water, and determine the iron as in § 113, 3, *a*. The difference gives the quantity of the alumina. If any silicic acid remains behind on dissolving the precipitate, it is to be collected on a filter, ignited, weighed, and deducted from the alumina. The filtrate contains the manganese, the alkaline earths, and the alkalies. Precipitate the manganese with sulphide of ammonium (§ 109, 2), boil with hydrochloric acid and filter off the sulphur, precipitate the lime, after addition of ammonia, with oxalate of ammonia, and lastly, after removing the ammonia salts by ignition, precipitate the magnesia from the hydrochloric acid solution of the residue with double phosphate of soda and ammonia. However, if it is intended to estimate the alkalies, the magnesia must be separated by one of the processes in § 153, 4. This method is convenient, and gives good results, especially in the presence of much iron and little alumina. Since alumina is not precipitated by alkaline acetates or formates with the same certainty as iron, it is necessary to test the weighed sulphide of manganese for alumina. **113**

3. *Method based upon the application of Sulphide of Ammonium.*

Mix the fluid in a flask with chloride of ammonium, then with ammonia, until a precipitate just begins to form, then with yellow sulphide of ammonium, fill the flask nearly up to the top with water, cork it, allow to settle in a warm place, filter, and wash the precipitate—consisting of sulphides of iron and manganese and hydrate of alumina—without interruption with water containing sulphide of ammonium. Separate the lime, magnesia, and **114** alkalies in the filtrate as in **113**. Dissolve the precipitate in hydrochloric acid, and separate the alumina from the iron and manganese according to **77** or **78**, and then the iron from the manganese, say by **82** or **85**.

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* In cases where it is intended to estimate the alkalies in the filtrate, ammonia salts must be used instead of the soda salts.

The following methods are particularly suitable in cases where no manganese is present, or only inappreciable traces:—

4. *Methods based upon the application of Ammonia.*

a. The solution must contain all the iron in the state of sesquioxide. Add a relatively large quantity of chloride of ammonium, and—observing the precautions indicated in **45**—precipitate with ammonia. The precipitate contains the whole of the iron and alumina; at most an inappreciable amount of the latter remains in solution if the free ammonia has been almost but not entirely driven off by heat, if the solution was diluted sufficiently, and if enough chloride of ammonium was present. It may also contain small quantities of lime and magnesia and a little protosesquioxide of manganese. It is well, therefore, usually to redissolve the washed precipitate in hydrochloric acid, and reprecipitate with ammonia. In this way the precipitate will be got free from alkaline earths and manganese. Wash the precipitate completely, dry, ignite, and treat according to **113**. If silicic acid remains undissolved, it is to be determined and deducted. The solution filtered from the alumina and sesquioxide of iron is concentrated by evaporation, the manganese is precipitated and determined according to § 109, 2, as sulphide, the alkaline earths and alkalies in the filtrate are estimated according to **113**. The weighed sulphide of manganese is digested with dilute hydrochloric acid, any residue that may remain fused with bisulphate of potassa, dissolved in water, and tested for alumina. **115**

b. Precipitate the alumina, sesquioxide of iron, and lime, by addition of ammonia and carbonate and oxalate of ammonia altogether, decant, and filter. Dissolve the precipitate in hydrochloric acid, add tartaric acid, to prevent the precipitation of sesquioxide of iron and alumina, and then precipitate the lime with ammonia as oxalate. Filter, and separate the iron from the alumina in the filtrate as in **77**; and the magnesia and alkalies in the first filtrate as in **18**. Should the first filtrate contain sulphuric acid, remove this by chloride of barium, then separate the alkaline earths from the alkalies by evaporation with oxalic acid, ignition, and treatment of the residue with boiling water, and finally the baryta from the magnesia as in **29** (E. MITSCHERLICH; LEWINSTEIN*). As alumina in presence of oxalate of ammonia is only precipitated gradually on warming (PISANI), it is necessary to digest some time in the heat before the first filtration, and as a portion of the magnesia is always present in the precipitate, I would recommend, after separating the iron from the alumina, to test the fluid filtered from the latter, and also the alumina itself for magnesia. The method cannot be applied in the presence of weighable quantities of manganese. **116**

c. Precipitate with ammonia, digest for some time in the heat, till the excess of ammonia is in a great measure removed, filter, **117** wash carefully, dry and ignite; add, without reducing the residue to powder, at least 10 times the quantity of anhydrous carbonate of soda, cover the crucible, and heat the mixture over the blast gas-lamp, or some other appropriate source of heat (the heat of a spirit lamp with double draught is not sufficiently powerful), until decomposition of the carbonate of soda is no longer observable, for at least 45 minutes. Boil the fused mass, best in a silver dish, after addition of some caustic potassa, with water until thoroughly extracted; add, if manganate of soda imparts a green tint to the solution, a few drops of alcohol, and wash the precipitate by decantation and filtration, first with water containing potassa, then with pure water. Dissolve the precipitate in hydrochloric acid, heat with a few drops of alcohol, to facilitate the reduction of the sesquichloride of manganese, and separate finally, by means of acetate of ammonia, the sesquioxide of iron from the portions of manganese, lime and magnesia contained in the ammonia precipitate, which may then be estimated either separately or jointly with the principal quantities according to **113**. The alumina is determined in the alkaline solution as in **78** (R. RICHTER[*]).

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* Journ. f. prakt. Chem. 68, 99.

5. *Method based upon the Decomposition of the Nitrates* (DEVILLE'S *method*).

This method presupposes that the bases are combined with nitric acid only. **118**

Proceed first as in **46**. The escape of the nitrous acid fumes, observed during the heating of the nitrates, is no proof of the total decomposition of the nitrates of iron and alumina, as these vapors may owe their formation to the conversion of the nitrate of protoxide of manganese into binoxide. Stop the application of heat when no more vapors are evolved, and the substance has acquired a uniform black color. After the treatment with nitrate of ammonia, the solution contains nitrates of lime, magnesia and the alkalies, the residue contains alumina, sesquioxide of iron, binoxide of manganese and—in the presence of much manganese—small quantities of the alkaline earths. (That some manganese is dissolved, under certain circumstances, has been stated already in **71**; *this trace is found with the magnesia, and finally separated from the latter*).

DEVILLE recommends the following methods to effect the further separation of the bases:—

a. Heat the *residue* with moderately strong nitric acid, until the alumina and sesquioxide of iron are dissolved, leaving the residuary binoxide of manganese of a pure black color. Ignite the residue, and weigh the protosesquioxide of manganese formed. Evaporate the solution in a platinum crucible, ignite, and weigh the mixture of sesquioxide of iron and alumina, which may possibly also contain some protosesquioxide of manganese. Treat a portion of it by the method described in **91**; this gives the alumina. If manganese was present, the iron cannot be estimated by difference. DEVILLE therefore evaporates the solution of the protochlorides (**92**) with sulphuric acid, ignites gently, and treats the residue, which consists of sesquioxide of iron and some sulphate of protoxide of manganese, with water to dissolve the latter. (Should the heat applied have been too strong, which might possibly lead to the decomposition also of sulphate of protoxide of manganese, the residue is moistened with a mixture of oxalic and nitric acids, some sulphuric acid added, and the process repeated.)

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[*] Journ. f. prakt. Chem. 64, 378.

b. From the *filtrate*, precipitate first the lime by oxalate of ammonia, then separate the magnesia from the alkalies as directed § 153, 4.

This method is not to be recommended in the presence of manganese.

6. *Method which combines* 4 *and* 5.

Precipitate with ammonia (**45**), decant, filter, wash, remove the still moist precipitate, as far as practicable, from the filter, dissolve the rest in nitric acid, transfer this to the dish, to effect also the solution of the bulk of the precipitate; proceed as in **118**, and add the fluid, separated from the sesquioxide of iron and alumina, and still containing small quantities of magnesia, and possibly traces of lime, to the principal filtrate. This method is to be recommended in the absence of manganese. The determination of the alumina is best effected by estimating the total amount of sesquioxide of iron and alumina, then the sesquioxide of iron volumetrically (**104**). If on dissolving the precipitate of sesquioxide of iron and alumina any silica remains, this must be deducted. **119**

Supplement to the Fourth Group.

To §§ 158, 159, 160.

SEPARATION OF SESQUIOXIDE OF URANIUM FROM THE OTHER OXIDES OF GROUPS I.—IV.

120 It has already been stated, in § 114, that sesquioxide of uranium cannot be completely separated from the *alkalies* by means of ammonia, as the precipitated ammonio-sesquioxide of uranium is likely to contain also fixed alkalies. The precipitate should therefore be dissolved in hydrochloric acid, the solution evaporated in the platinum crucible, the residue gently ignited in a current of hydrogen gas (see fig. 79, p. 200), the chlorides of the alkali metals extracted with water, and the protoxide of uranium ignited in hydrogen, in order to its being weighed as such, or in the air, whereby it is converted into protosesquioxide. Instead of dissolving the precipitate in hydrochloric acid and treating the solution as directed, you may heat the precipitate cautiously* with chloride of ammonium, and treat the residue with water (H. ROSE). Uranium may be completely separated from the alkalies also by sulphide of ammonium as H. ROSE found. REMELɆ has examined this subject with great care and recommends the following method of precipitation:—The solution being *neutral or slightly acid*, add an excess of yellow sulphide of ammonium and keep nearly boiling for an hour to convert the first formed precipitate of oxysulphide of uranium entirely into a mixture of protoxide of uranium and sulphur. The fluid at first dark from presence of dissolved uranium will now appear yellow and transparent. Filter off the precipitate containing all the uranium and wash it with cold or warm water, first by decantation finally on the filter. It is well to mix a little sulphide or chloride of ammonium with the water, as when pure water is used the last filtrate is apt to be turbid. The dried precipitate is roasted and then converted into protosesquioxide by ignition in the air, or into protoxide by ignition in hydrogen (§ 114).

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* Strong ignition would occasion the volatilization of chloride of uranium.

† Zeitschr. f. anal. Chem. 4, 379.

121 Fr. Stolba* recommends to separate sesquioxide of uranium from the alkalies by precipitating the latter in the form of silicofluorides with addition of alcohol. Treat the substance with aqueous hydrofluosilicic acid of 3 to 5 per cent. and warm gently. As soon as the yellow powder has disappeared, allow to cool, add 3 to 4 volumes of spirit of wine of 75 to 80 per cent., mix, and allow to settle in a dark place, or at least in a place unexposed to direct sunlight, filter, wash with spirit till the washings are completely free from acid reaction, and determine the alkali volumetrically according to § 97, 5. Direct sunlight renders the alcoholic solution of uranium turbid, causing separation of green protosilicofluoride of uranium. To estimate the uranium also, evaporate the alcoholic filtrate, heat the residue with excess of sulphuric acid to remove the hydrofluosilicic acid, dissolve with the aid of a little nitric acid in water, filter, and estimate the uranium in the filtrate by § 114.

The method can also be used for the analysis of sesquisalts of uranium containing alkali and soluble in spirits of wine. Moderate quantities of hydrochloric or nitric acid do not interfere, while sulphuric acid causes the alkali to be too low in consequence of the coprecipitation of alkaline sulphate.

122 From *baryta*, sesquioxide of uranium may be separated by sulphuric acid, from *strontia* and *lime*, by sulphuric acid and alcohol. Ammonia fails to effect complete separation of sesquioxide of uranium from the alkaline earths, the precipitate always containing not inconsiderable quantities of the latter. In such precipitates, however, the uranium and the alkaline earth may likewise be separated by gentle ignition with chloride of ammonium and treatment of the residue with water.

123 Uranium may be separated from *strontia* and *lime* also by precipitation with sulphide of ammonium by the method given above in the separation from the alkalies. As alkaline earthy carbonates may be coprecipitated, treat the washed precipitate of protoxide of uranium and sulphur *in the cold* with dilute hydrochloric acid which will not dissolve protoxide of uranium. Sulphide of ammonium will not answer for the separation of uranium from *baryta* (Remelé†).

124 *Magnesia* may be separated from sesquioxide of uranium not only by sulphide of ammonium in presence of chloride of ammonium, but also by ammonia. Add enough chloride of ammonium to the solution, heat to boiling, supersaturate with ammonia, continue boiling till the odor of ammonia is but slight, filter the hot fluid, and wash the precipitate, which is free from magnesia, with hot water containing ammonia (H. ROSE). It is always well to test the protoxide of uranium obtained by ignition in hydrogen for magnesia by treating with dilute hydrochloric acid.

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* Zeitschrift f. analyt. Chem. 3, 71.

† *Ib.* 4, 383.

Alumina is best separated from sesquioxide of uranium by mixing the somewhat acid fluid with carbonate of ammonia in excess. The sesquioxide of uranium passes completely into solution, while the alumina remains absolutely undissolved. Filter, evaporate, add hydrochloric acid to resolution of the precipitate produced, heat till all the carbonic acid is expelled, and precipitate with ammonia (§ 114).

Sesquioxide of uranium is best separated from *sesquioxide of chromium* (W. GIBBS*) by adding to the solution soda in slight excess, heating to boiling and adding bromine water, when the sesquioxide of chromium is rapidly converted into chromic acid. Filter the solution containing chromate of soda from the precipitate which has a deep orange red color and consists of a compound of soda and sesquioxide of uranium mixed with some chromate of sesquioxide of uranium. Wash the precipitate with hot water containing a little soda, dissolve it in hot nitric acid, boil the solution a few minutes to drive off any nitrous acid and precipitate the chromic acid according to § 130, I, *a*, *β* with protonitrate of mercury (according to GIBBS at a boiling heat). The filtrate now contains the whole of the uranium, of course in presence of mercury.

The separation of uranium from the metals of the *fourth group* may be based simply on the fact that carbonate of ammonia prevents the precipitation of uranium but not that of the other metals by sulphide of ammonium. Mix the solution with a mixture of carbonate of ammonia and sulphide of ammonium, allow to subside in a closed flask and wash the precipitate with water containing carbonate of ammonia and sulphide of ammonium. **125**

Remove the greater part of the excess of carbonate of ammonia from the filtrate by a very gentle heat, acidify with hydrochloric acid, warm, filter off the separated sulphur and throw down the uranium either by sulphide of ammonium (see above, *Separation of Uranium from the Alkalies*) or by heating with nitric acid and then adding ammonia (H. ROSE†, REMELÉ‡). The method is not so suitable in presence of nickel, as a little of this metal is very liable to pass into the filtrate on precipitation with carbonate of ammonia and sulphide of ammonium.

Sesquioxide of iron may be also separated from sesquioxide of uranium by means of an excess of carbonate of ammonia. The small quantity of iron which passes with the uranium into solution will fall down on allowing the solution to stand for several hours, or it may be precipitated with sulphide of ammonium, before the uranium is thrown down (PISANI§).

From *protoxides of nickel, cobalt, and manganese, oxide of zinc* and *magnesia*, the sesquioxide of uranium may also be separated by carbonate of baryta. The fluid, which should contain a little free acid, is mixed with the precipitant in excess, and allowed to stand in the cold for 24 hours with frequent shaking (**76**).

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* Zeitschrift f. analyt. Chem. 12, 310. † *Ib.* 1, 412. ‡ *Ib.* 4, 385.
§ Compt. rend. 52, 106.

From *cobalt*, *nickel* and *zinc* uranium may also be separated (GIBBS and PERKINS*) by taking the neutral or slightly acid solutions of the chlorides, adding acetate of soda in excess and a few drops of acetic acid, and passing a rapid current of hydrosulphuric acid for half an hour through the boiling fluid The uranium remains dissolved while the other metals are precipitated. I should advise testing the filtrate with a mixture of carbonate of ammonia and sulphide of ammonium to see if any nickel, cobalt or zinc remain in solution. **126**

FIFTH GROUP.

OXIDE OF SILVER—SUBOXIDE OF MERCURY—OXIDE OF MERCURY—OXIDE OF LEAD—TEROXIDE OF BISMUTH—OXIDE OF COPPER—OXIDE OF CADMIUM.

I. SEPARATION OF THE OXIDES OF THE FIFTH GROUP FROM THOSE OF THE FIRST FOUR GROUPS.

§ 162.

Index :—The Nos. refer to those in the margin.

Oxide of silver from the oxides of Groups I.—IV., 127, 128.
Oxide and suboxide of mercury from the oxides of Groups I.—IV., 127, 129.
Oxide of lead from the oxides of Groups I.—IV., 127, 130.
,, protoxide of manganese, 142.
Teroxide of bismuth from the oxides of Groups I.—IV., 127, 140.
,, protoxide of manganese, 142.
Oxide of copper from the oxides of Groups I.—IV., 127, 131—135.
,, oxide of zinc, 136, 137.
,, protoxide of manganese, 142.
,, sesquioxide of iron, 138.
,, protoxide of nickel, 139.
Oxide of cadmium from the oxides of Groups I.—IV., 127.
,, oxide of zinc, 141.
,, protoxide of manganese, 142.

A. *General Method.*

ALL THE OXIDES OF THE FIFTH GROUP FROM THOSE OF THE FIRST FOUR GROUPS.

Principle: Sulphuretted Hydrogen precipitates from Acid Solutions the Metals of the Fifth Group, but not those of the first Four Groups.

The following points require especial attention in the execution of the process :— **127**

a. To effect the separation of the oxides of the fifth group from those of the first three groups, by means of sulphuretted hydrogen, it is necessary simply that the reaction of the solution should be acid, the nature of the acid to which the reaction is due being of no consequence. But, to effect the separation of the oxides of the fifth group from those of the fourth, the presence of a free mineral acid is indispensable; otherwise, zinc and, under certain circumstances, also cobalt and nickel may be coprecipitated.

β. But even the addition of hydrochloric acid to the fluid will not always entirely prevent the coprecipitation of the zinc. RIVOT and BOUQUET[*] declare a complete separation of copper from zinc by means of sulphuretted hydrogen, altogether impracticable. CALVERT[†] states that he has arrived at the same conclusion. On the other hand, SPIRGATIS[‡] concurs with H. ROSE in maintaining that complete separation of copper from zinc may be effected by means of sulphuretted hydrogen, in presence of a sufficient quantity of free acid.

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* Zeitschr. f. anal. Chem. 3, 334.

In this conflict of opinions, I thought it necessary to subject this method once more to a searching investigation. I therefore instructed one of the students in my laboratory, Mr. GRUNDMANN, to make a series of experiments in the matter, with a view to settling the question.[§]

The following process is founded on the results which we obtained:—

Add to the COPPER and ZINC solution a large amount of hydrochloric acid (*e.g.*, to ·4 grm. oxide of copper in 250 c.c. of solution, 30 c.c. hydrochloric acid of 1·1 sp. gr.), conduct into the fluid at about 70° sulphuretted hydrogen largely in excess, filter before the excess of sulphuretted hydrogen has had time to escape or become decomposed, wash with sulphuretted hydrogen water, dry, roast, redissolve in nitrohydrochloric acid, evaporate nearly to dryness, add water and hydrochloric acid as above, and precipitate again with sulphuretted hydrogen. This second precipitate is free from zinc; it is treated as directed in § 119, 3.

If CADMIUM is present, it is well to have less acid present, *e.g.*, to ·4 grm. oxide of cadmium in 250 c.c. of solution add 10 c.c. hydrochloric acid of 1·1 sp. gr. If the quantity of zinc is considerable, dissolve the first precipitate of sulphide of cadmium in hot hydrochloric acid, evaporate nearly to dryness, add 10 c.c. hydrochloric acid and about 250 c.c. water, and precipitate again. In this way the results are quite satisfactory.

γ. The other metals of the fifth group comport themselves in this respect similarly to cadmium, *i.e.*, they are not completely precipitated by sulphuretted hydrogen in presence of too much free acid in a concentrated solution. Lead requires the least amount of free acid to be retained in solution; then follow in order of succession, cadmium, mercury, bismuth, copper, silver (M. MARTIN[‖]). A portion of the filtrate should, if necessary, be tested by addition of a large quantity of sulphuretted hydrogen to see if the precipitation of the fifth group was complete.

δ. If hydrochloric acid produces no precipitate in the solution, it is preferred as acidifying agent, otherwise sulphuric or nitric acid must be used. In the latter case the fluid must be rather largely diluted. ELIOT and STORER[¶] arrived at the same conclusion as ourselves, and showed that the cause of CALVERT'S unfavorable results was the too large dilution of his solutions. For to prevent the precipitation of zinc you have not merely to preserve a certain proportion between the zinc and the free acid, but also a certain degree of dilution. Although I agree with the above-named chemists in the opinion that it is possible to produce a condition of the fluid, under which one precipitation will effect complete separation, still it appears to me better, for practical purposes, to precipitate twice, as this is sure to lead to the desired result.

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[*] Annal. d. Chem. u. Pharm. 80, 364.
[†] Journ. f. prakt. Chem. 71, 155.
[‡] *Ib.* 57, 184.
[§] *Ib.* 73, 241.
[‖] *Ib.* 67, 371.
[¶] On the Impurities of Commercial Zinc, &c.—Memoirs of the American Academy of Arts and Sciences. New Series. Vol. 8.

ε. A somewhat copious experience in the separation of COPPER from NICKEL (and COBALT) which so frequently occurs, has led me to the opinion that a double precipitation is unnecessary. If the solution which is to be treated with sulphuretted hydrogen contains enough free hydrochloric acid and not too much water, the copper falls down absolutely free from nickel, while, on the other hand, if the quantity of free acid is not too large, the filtrate will be quite free from copper. The method given in β for separating copper from zinc is also to be recommended in this case.

ζ. CADMIUM and ZINC may, according to FOLLENIUS, also be completely separated by a single precipitation, if the metals are present in a sulphuric acid solution containing 25 or 30 per cent. of dilute acid of 1·19 sp. gr. Precipitate with sulphuretted hydrogen at 70°. Collect the precipitate on a weighed asbestos filter (§ 47, end), dry in a current of heated air, ignite gently in a stream of pure sulphuretted hydrogen (to convert small quantities of sulphate of cadmium into sulphide), remove the small quantity of separated sulphur by gentle ignition in a current of air, and weigh.

B. *Special Methods.*

SINGLE OXIDES OF THE FIFTH GROUP FROM SINGLE OR MIXED OXIDES OF THE FIRST FOUR GROUPS.

1. SILVER is most simply and completely separated from the OXIDES OF THE FIRST FOUR GROUPS by means of hydrochloric acid. The hydrochloric acid must not be used too largely in excess, and the fluid must be sufficiently dilute; otherwise a portion of the silver will remain in solution. Care must be taken also not to omit the addition of nitric acid, which promotes the separation of the chloride of silver. The latter should be treated according to § 115, 1, *a*. **128**

2. The separation of MERCURY from the METALS OF THE FIRST FOUR GROUPS may be effected also by ignition, which will cause the volatilization of the mercury or the mercurial compound, leaving the non-volatile bodies behind. The method is applicable in many cases to alloys, in others to oxides, chlorides, or sulphides. If the mercury is estimated only from the loss, the operation is conducted in a crucible; otherwise in a bulb-tube, or a wide glass tube with porcelain boat. In the latter case it is well to use a current of hydrogen (compare § 118, 1, *a*; also *Examination of Mercurial Ores* in the Special Part). **129**

The precipitation of mercury as subchloride with phosphorous acid, according to § 118, 2, is also well adapted for its separation from metals of the first four groups. If the mercury is already present as suboxide, it may be separated and determined in a simple manner, by precipitation with hydrochloric acid (§ 117, 1).

3. FROM THOSE BASES WHICH FORM SOLUBLE SALTS WITH SULPHURIC ACID, OXIDE OF LEAD may be readily separated by that acid. The results are very satisfactory, if the rules given in § 116, 3, are strictly adhered to. 130

If you have lead in presence of baryta, both in form of sulphates, digest the precipitate with a solution of ordinary sesquicarbonate of ammonia, without application of heat. This decomposes the lead salt, leaving the baryta salt unaltered. Wash, first with solution of carbonate of ammonia, then with water, and separate finally the carbonate of lead from the sulphate of baryta, by acetic acid or dilute nitric acid (H. ROSE*). The same object may also be attained by suspending the washed insoluble salts in water and digesting with a clear concentrated solution of hyposulphite of soda at 15—20° (not higher). The sulphate of baryta remains undissolved, the sulphate of lead dissolves. Determine the lead in the filtrate (after § 116, 2) as sulphide of lead (J. LÖWE†). The method recommended by RIVOT, BEUDANT, and DAGUIN,‡ for separating the lead by mixing the solution with acetate of soda, heating and passing chlorine, requires, according to H. ROSE,§ to be executed with great caution, since portions of other oxides, even such as are not converted by chlorine into higher oxides—for instance, oxide of zinc—are very liable to be precipitated with the binoxide of lead.

4. OXIDE OF COPPER FROM ALL OXIDES OF THE FIRST FOUR GROUPS.

a. Free the solution as far as possible from hydrochloric and nitric acids by evaporation with sulphuric acid. Dilute if necessary, boil, and add *hyposulphite of soda*‖ as long as a black precipitate continues to form. As soon as this has deposited, and the supernatant fluid contains only suspended sulphur, the whole of the copper is precipitated. The precipitate is subsulphide of copper (Cu_2S), and may be readily washed without suffering oxidation. Convert it into anhydrous subsulphide by ignition in hydrogen (§ 119, 3). The other bases are in the filtrate and washings. Evaporate with some nitric acid, filter, and estimate the oxides in the filtrate.¶ Results good. The method requires practice, as the end of the precipitation of the copper is not so easy to hit as when sulphuretted hydrogen is employed. 131

If the solution contained hydrochloric or nitric acid, and this was not first removed before the addition of the hyposulphite, the precipitant would be required in much larger quantity; in the presence of hydrochloric acid because the subchloride of copper produced is only decomposed by a large excess of hyposulphite, in

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[*] Journ. f. prakt. Chem. 66, 166.

[†] *Ib.* 77, 75.

[‡] *Ib.* 61, 136.

[§] Pogg. Annal. 110, 417.

[‖] The commercial salt is often not sufficiently pure; in which case some carbonate of soda must be added to its solution, and the mixture filtered.

[¶] As far back as 1842, C. HIMLY made the first proposal to employ hyposulphite of soda for the precipitation of many metals as sulphides (Annal. d. Chem. u. Pharm. 43, 150). The question, after long neglect, was afterwards taken up again by VOHL (Annal. d. Chem. u. Pharm. 96, 237), and SLATER (Chem. Gaz. 1855, 369). FLAJOLOT, however, made the first quantitative experiments (Annal. des Mines, 1853, 641; Journ. f. prakt. Chem. 61, 105). The results obtained by him are perfectly satisfactory.

the presence of nitric acid because the hyposulphite does not begin to act on the copper salt till all the nitric acid is decomposed.

b. Precipitate the copper as *subsulphocyanide* according to § 119, 3, *b*, or 4, *e*; the other metals remain in solution (RIVOT). If alkalies were present and it were desired to determine them in the filtrate, sulphocyanide of ammonium must be used instead of the potassium salt usually employed. This method is particularly well adapted for the separation of copper from zinc. The zinc can be precipitated at once from the filtrate by carbonate of soda. The method is also suitable for separating copper from iron (H. ROSE*); in this case it is unnecessary that the sesquioxide of iron be completely reduced by the sulphurous acid added; the separation may be effected, even if the solution becomes blood-red on the addition of the precipitant. 132

c. The method of precipitating the copper by addition of a solution of iodine in sulphurous acid, after removal of the greater portion of the free acid present and addition of sulphurous acid which has been so often recommended, and was proposed by FLAJOLOT,† has been declared by H. ROSE‡ to give inaccurate results, because a not inconsiderable amount of copper remains in solution. This difficulty may be avoided by adding to the hydrochloric solution containing a slight excess of acid protochloride of tin in excess, chloride of ammonium, and then iodide of potassium, till the latter just predominates (E. FLEISCHER§). As, however, the filtrate will contain the excess protochloride of tin and the bichloride produced, which would have to be removed before the bases of groups 1—4 could be determined, this method offers no advantages. 133

d. If the solution is not too dilute, if the bases are present as sulphates, and if hydrochloric and nitric acids are absent, the copper may also be completely thrown down by *alkaline hypophosphite*. Hydride of copper is precipitated at about 70°, and this at a higher temperature, which should not be allowed to exceed 90°, is decomposed into copper and hydrogen. The precipitation is completed when a drop taken out is not coloured brown by sulphuretted hydrogen. Wash the spongy copper by decantation, dry it, and ignite in a current of hydrogen. The separation is thorough (W. GIBBS and R. CHAUVENET‖). The method is particularly useful for separating copper from the metals of Group 4, which may then be thrown down from the filtrate by sulphide of ammonium. 134

e. The solution should be free from hydrochloric acid, and should contain a certain quantity of free nitric acid (20 c.c. nitric acid of 1·2 sp. gr. to 200 c.c.), and some sulphuric acid. Throw down the copper by a galvanic current, so that the metal may be firmly deposited on a platinum vessel (preferably a platinum cone), which forms the negative pole. Take care that the current is strong enough, and, without interrupting it, remove the cone from the fluid occasionally to see when the copper is all precipitated. With proper execution the separation of copper from all metals of Groups 1—4 is thorough. All metals of Groups 1—4 remain dissolved, except manganese, which separates as binoxide at the positive pole. The method requires practice and strict attention to 135 the conditions which have been determined by a long course of experiments. It is particularly suited for mining assays and manufactures. The electrolytic method of separating copper was, I believe, first recommended by Gibbs,[*] and afterwards improved by Luckow.[†] Lecoq de Boisbaudran,[‡] Ullgren,[§] and Merrick[||] have also written on this subject. Finally the method was very accurately and minutely described by the Mansfelder Ober-Berg- und Hüttendirection at Eisleben,[¶] who, after giving a prize to Luckow's method, afterwards adopted it, and still further improved it. I must refer the reader for details to the last mentioned memoir and Luckow's paper.

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* Pogg. Annal. 110, 424.

† Annal. des Mines, 1853, 641.

‡ Pogg. Annal. 110, 425.

§ Zeitschr. f. anal. Chem. 9, 256.

‖ *Ib.* 7, 256.

5. Oxide of Copper from Oxide of Zinc.

a. Bobierre[**] employed the following method with satisfactory results in the analysis of many alloys of zinc and copper:— The alloy is put into a porcelain boat lying in a porcelain tube, and heated to redness for three-quarters of an hour at the most, a rapid stream of hydrogen gas being conducted over it during the process. The zinc volatilizes, the copper remains behind. If the alloy contains a little lead (under 2 to 3 per cent.) this goes off entirely with the zinc, and is partly deposited in the porcelain tube in front of the boat; if more lead is present part only is volatilized, the rest remaining with the copper (M. Burstyn[††]). **136**

b. A. W. Hofmann's method given below (**159**) for separating copper and cadmium, namely, boiling the precipitated sulphides with dilute sulphuric acid, is also adapted for separating copper and zinc (G. C. Wittstein[‡‡]). **137**

6. Oxide of Copper from Sesquioxide of Iron.

One of the oldest methods for separating these oxides consists in precipitating the solution with ammonia and filtering off the oxide of iron from the ammoniacal solution of oxide of copper. To obtain accurate results, however, the precipitation must be repeated according to the quantity of copper, two or three times— in fact, till the filtrate no longer appears blue, otherwise the sesquioxide of iron will contain copper. **138**

7. Oxide of Copper from Protoxide of Nickel.

Evaporate the nitric acid solution, if such is given, with addition of hydrochloric acid, to dryness, dissolve the chlorides in water, add about twice the quantity of the metals present of pure bitartrate of potassa, warm slightly, to favor solution, and add a solution of potassa in alcohol gradually, till the first-formed precipitate, consisting of hydrated oxides, has redissolved. After cooling add a solution of pure grape sugar and boil for 1 or 2 minutes. The copper falls down as suboxide. After you have satisfied yourself, by the addition of a drop of sugar solution to the clear fluid, that the precipitation is complete, filter, and deter- **139** mine the copper either as oxide (by ignition, treatment with nitric acid and reignition) or as subsulphide (§ 119, 3, *c*) or volumetrically (§ **119**, 4, *c*). The fluid containing the nickel is evaporated to dryness, the residue ignited, the carbonate of potassa removed by washing, the residue reignited, dissolved in aqua regia, and the nickel precipitated by potassa according to § 110, 1, *a* (DE-WILDE*). The oxide of copper must be filtered off and washed rapidly, otherwise a part will be redissolved; the method is troublesome and by no means more accurate than the separation by sulphuretted hydrogen.

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[*] Zeitschr. f. anal. Chem. 3, 334.

[†] Dingler's polyt. Journ. 177, 296 and (in detail), Zeitschr. f. anal. Chem. 8, 25.

[‡] Zeitschr. f. anal. Chem. 7, 253, and 9, 102.

[§] *Ib.* 7, 255.

[||] American Chemist, 2, 136.

[¶] Zeitschr. f. anal. Chem. 11, 1.

[**] Compt. rend. 36, 224; Journ. f. prakt. Chem. 58, 380.

[††] Zeitschr. f. anal. Chem. 11, 175.

[‡‡] Vierteljahrsschr. f. prakt. Pharm. 17, 461; Zeitschr. f. anal. Chem. 8, 202.

8. TEROXIDE OF BISMUTH FROM THE OXIDES OF THE FIRST FOUR GROUPS, WITH THE EXCEPTION OF SESQUIOXIDE OF IRON.

Precipitate the bismuth according to § 120, 4, as basic chloride, **140** and determine it as metal; all the other bases remain completely in solution. Results very satisfactory (H. ROSE†).

9. OXIDE OF CADMIUM FROM OXIDE OF ZINC.

Prepare a hydrochloric or nitric acid solution of the two oxides, **141** as neutral as possible, add a sufficient quantity of tartaric acid, then solution of potassa or soda, until the reaction of the clear fluid is distinctly alkaline. Dilute now with a sufficient quantity of water, and boil for 1½–2 hours. All the cadmium precipitates as hydrated oxide free from alkali (to be determined as directed § 121), whilst the whole of the zinc remains in solution; the latter metal is determined as directed in § 108, 1, *b* (AUBEL and RAMDOHR‡). The test-analyses communicated are satisfactory. As the separation only succeeds when the substances are present in correct proportions, I will add the quantities employed by AUBEL and RAMDOHR with especially good effect. About 1 grm. oxide of zinc and 1 grm. oxide of cadmium were dissolved in hydrochloric acid, 30 grm. solution of tartaric acid (containing ·23 grm. acid in 1 grm.), 50 grm. soda solution of 1·16 sp. gr., and 120 grm. water added, and the whole boiled 2 hours. (The boiling must on no account be done in glass, a platinum or silver dish should be used.)

10. PROTOXIDE OF MANGANESE FROM OXIDE OF LEAD, TEROXIDE OF BISMUTH, OXIDE OF CADMIUM, AND OXIDE OF COPPER.

If you have a solution containing protoxide of manganese and **142** one of the other bases, precipitate the hot solution with carbonate of soda, wash the precipitate with boiling water, first by decantation, then on the filter, dry, ignite some time, weigh, and determine, in a portion of the residue, the manganese by the volumetric method (**72**). If the oxide of lead, of copper, of cadmium, or the teroxide of bismuth is present in sufficient quantity, the residue has the formula $Mn_2O_3 + xMO$ or $Mn_2O_3xBiO_3$ (KRIEGER§). You must never omit adding some sulphide of ammonium to the filtrate, to ascertain whether the oxides have been entirely precipitated by carbonate of soda.

In precipitating copper by alkaline carbonates the fluid must be diluted so that 1 litre may not contain more than 1 grm. copper, the precipitant must be added in slight excess, and the mixture boiled for about half an hour, when the bluish-green basic carbonate will become dark, granular, and easy to wash (W. GIBBS and E. R. TAYLOR*).

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* Chem. News, 7, 49.

† Pogg. Annal. 110, 429.

‡ Annal. d. Chem. u. Pharm. 103, 33.

§ *Ib.* 87, 264.

II. SEPARATION OF THE OXIDES OF THE FIFTH GROUP FROM EACH OTHER.

§ 163.

Index :—The Nos. refer to those in the margin.

Oxide of silver from oxide of copper, 143, 148, 150, 164, 165.
,, oxide of cadmium, 143, 148, 150.
,, teroxide of bismuth, 143, 147, 150, 161.
,, oxide of mercury, 143, 148, 150, 158, 160.
,, oxide of lead, 143, 146, 147, 150, 155, 164, 165.
Oxide of mercury from oxide of silver, 143, 148, 150, 158, 160.
,, suboxide of mercury, 144.
,, oxide of lead, 145, 146, 147, 150, 158, 160.
,, teroxide of bismuth, 145, 147, 150, 151, 158.
,, oxide of copper, 145, 149, 150, 158, 160.
,, oxide of cadmium, 145, 150, 158.
Suboxide of mercury from oxide of mercury, 144.
,, oxide of copper, 144.
,, oxide of cadmium, 144.
,, oxide of lead, 144, 146.
Compare, also, Oxide of mercury from the other metals.
Oxide of lead from oxide of silver, 143, 147, 150, 155, 164, 165.
,, oxide of mercury, 145, 146, 147, 150, 158, 160.
,, suboxide of mercury, 144, 146.
,, oxide of copper, 146, 147, 150, 152.
,, teroxide of bismuth, 146, 147, 152, 161, 162.
,, oxide of cadmium, 146, 147, 150.
Teroxide of bismuth from oxide of silver, 143, 147, 150, 161.
,, oxide of lead, 146, 147, 152, 161, 162.
,, oxide of copper, 147, 150, 151, 153, 161.
,, oxide of cadmium, 147, 150, 151, 153, 157.
,, oxide of mercury, 145, 147, 150, 151, 158.
Oxide of copper from oxide of silver, 143, 148, 150, 164, 165.
,, oxide of lead, 146, 147, 150, 152.
,, teroxide of bismuth, 147, 150, 151, 153, 161.
,, oxide of mercury, 145, 149, 150, 158, 160.
,, suboxide of mercury, 144.
,, oxide of cadmium, 149, 150, 152, 154, 156, 159.
,, suboxide of copper, 163, 165.
Oxide of cadmium from oxide of silver, 143, 148, 150.
,, oxide of lead. 146, 147, 150.
,, teroxide of bismuth, 147, 150, 151, 152, 157.
,, oxide of copper, 146, 150, 152, 154, 156, 159.
,, oxide of mercury, 145, 150. 158.
,, suboxide of mercury, 144.

1. *Methods based upon the Insolubility of certain of the Chlorides in Water or Spirit of Wine.*

a. OXIDE OF SILVER FROM OXIDE OF COPPER, OXIDE OF CADMIUM, TEROXIDE OF BISMUTH, OXIDE OF MERCURY, AND OXIDE OF LEAD.

a. To separate *oxide of silver* from *oxide of copper, oxide of* 143
cadmium, and *teroxide of bismuth,* add to the nitric acid solution containing excess of nitric acid, hydrochloric acid as long as a

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* Zeitschr. f. anal. Chem. 7, 258.

precipitate forms, and separate the precipitated chloride of silver from the solution which contains the other oxides, as directed § 115, 1, *a*. In the presence of bismuth, after pouring off the supernatant fluid, heat again with nitric acid, and wash with dilute nitric acid before washing with water.

β. If you wish to separate *oxide of mercury* from *oxide of silver* by hydrochloric acid, special precautions must be taken, as a solution of nitrate of mercury possesses the property of dissolving chloride of silver (WACKENRODER, V. LIEBIG,* H. DEBRAY†). Although the chloride of silver in solution for the most part separates on the addition of enough hydrochloric acid to convert the nitrate of mercury into chloride, or on addition of acetate of soda, still we cannot depend upon the complete precipitation of the silver. On this account, mix the nitric acid solution—which may not contain any suboxide of mercury, and is to be in a sufficiently dilute condition and acidified with nitric acid—with hydrochloric acid, as long as a precipitate forms. Allow to deposit, filter off the clear fluid, heat the precipitate—to free it from any possibly coprecipitated basic mercury salts—with a little nitric acid, add water, then a few drops of hydrochloric acid, and filter off the chloride of silver. In the filtrate determine the mercury as sulphide (§ 118, 3), and finally test this for silver, by ignition in a stream of hydrogen—any silver that may happen to be present will remain behind in the metallic state.

γ. In the separation of *silver* from *lead*, the precipitation is advantageously preceded by addition of acetate of soda. The fluid must be hot and the hydrochloric acid rather dilute; no more must be added of the latter than is just necessary. In this manner, the separation may be readily effected, since chloride of lead dissolves in acetate of soda (ANTHON.) The chloride of silver is washed with hot water. The lead is thrown down from the filtrate with sulphuretted hydrogen. If you desire to prevent the occasionally injurious influence of acetate of soda, great care must be given to the washing of the chloride of silver. It is also well to reduce the weighed chloride by gentle ignition in a current of hydrogen and to test the silver obtained for lead. Regarding the estimation of very minute quantities of silver in lead, compare Analysis of Refined Lead in the Special Part.

δ. The volumetric method (§ 115, 5) is usually resorted to in mints to determine the *silver in alloys*. In presence of oxide of mercury, acetate of soda is mixed with the fluid, immediately before the addition of the solution of chloride of sodium. In the East India mint the silver is separated and weighed as chloride.‡

b. SUBOXIDE OF MERCURY FROM THE OXIDES OF MERCURY, COPPER, CADMIUM, AND LEAD.

144 Mix the highly dilute cold solution with hydrochloric acid, as long as a precipitate (subchloride of mercury) forms; allow this to deposit, filter on a weighed filter, dry at 100°, and weigh. The filtrate contains the other oxides. If you have to analyse a solid body, insoluble in water, either treat directly, in the cold, with

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* Annal. d. Chem. u. Pharm. 81, 128.

† Compt. rend. 70, 847 ; Zeitschr. f. anal. Chem 13, 349.

‡ Chem. Centralbl. 1872, 202.

dilute hydrochloric acid, or dissolve in highly dilute nitric acid, and mix the solution with a large quantity of water before proceeding to precipitate. Care must always be taken that the mode of solution is such as not to endanger the oxidation of the suboxide of mercury. If lead is present the washing of the subchloride must be executed with special care with water of 60—70°, till the filtrate ceases to be colored with sulphuretted hydrogen. As an additional security, it is well to test at last whether the weighed subchloride leaves no sulphide of lead behind on cautious ignition with sulphur in a stream of hydrogen.

c. OXIDE AND SUBOXIDE OF MERCURY FROM OXIDE OF COPPER, OXIDE OF CADMIUM, AND (but less well) FROM TEROXIDE OF BISMUTH, AND OXIDE OF LEAD.

If mercury is present as oxide or as oxide and suboxide, it is **145** precipitated according to § 118, 2, by means of hydrochloric acid and phosphorous acid as subchloride. The precipitate, particularly when bismuth is present, is first washed with water containing hydrochloric acid, then with pure water, till the washings are no longer colored with sulphuretted hydrogen (H. ROSE*). In the presence of lead, the remarks in **144** must be attended to.

d. The method of separating oxide of lead from oxide of mercury, oxide of copper, and teroxide of bismuth, by highly concentrating the nitric acid solution, adding hydrochloric acid and alcohol, and washing the chloride of lead with alcohol, cannot be recommended. It is unequal in accuracy to the following method (**146**).

2. *Methods based upon the Insolubility of Sulphate of Lead.*

OXIDE OF LEAD FROM ALL OTHER OXIDES OF THE FIFTH GROUP.

Mix the nitric acid solution with pure sulphuric acid in not **146** too slight excess, evaporate until the sulphuric acid begins to volatilize, allow the fluid to cool, add water (in which, if there is a sufficient quantity of free sulphuric acid present, the sulphates of mercury and of bismuth dissolve completely), and then filter the solution, which contains the other oxides, *without delay* from the undissolved sulphate of lead. If it is feared that the residue no longer contains enough free sulphuric acid, add some dilute acid to it before adding the water. Wash the precipitate with water containing sulphuric acid, displace the latter with spirit of wine, dry, and weigh (§ 116, 3). Precipitate the other oxides from the filtrate by sulphuretted hydrogen. If *oxide of silver* is present in any notable quantity, this method cannot be recommended, as the sulphate of silver is not soluble enough. In this case you may follow ELIOT and STORER,† viz., mix the solution with nitrate of ammonia, warm, precipitate the greater portion of the silver with chloride of ammonium, evaporate the filtrate, remove the ammonia salts by ignition, and in the residue separate the small remainder of the silver from the lead with sulphuric acid as just directed.

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* Pogg. Annal. 110, 534.

† Proceedings of the American Academy of Arts and Sciences, Sept. 11, 1860, p. 52 : Zeitschr. f. anal. Chem. 1, 389.

For the separation of *lead from bismuth*, on the above principle, H. **Rose*** gives the following process as the best. If both oxides are in dilute nitric acid solution, as is usually the case, evaporate to small bulk, and add enough hydrochloric acid to dissolve all the teroxide of bismuth; the lead separates partially as chloride. Should a portion of the clear fluid poured off become turbid on the addition of a drop of water, you must add some more hydrochloric acid, till no permanent turbidity is produced unless several drops of water are added. The turbid fluids should all be returned, and the glasses rinsed with alcohol. Add now dilute sulphuric acid, allow to stand some time with stirring, add spirit of wine of ·8 sp. gr., stir well, allow to settle for a long time, filter, wash the sulphate of lead first with alcohol, mixed with a small quantity of hydrochloric acid, then with pure alcohol. Determine it after § 116, 3. Mix the filtrate at once with a large quantity of water, and proceed with the precipitated basic chloride of bismuth according to § 120, 4.

3. *Methods based upon the different Deportment of the Oxides and Sulphides, with Cyanide of Potassium* (FRESENIUS and HAIDLEN†).

a. OXIDE OF LEAD AND TEROXIDE OF BISMUTH FROM ALL OTHER OXIDES OF THE FIFTH GROUP.

Mix the *dilute* solution with carbonate of soda in *slight* excess, add solution of cyanide of potassium (free from sulphide), heat gently for some time, filter and wash. On the filter you have carbonate of lead and of bismuth (containing alkali); the filtrate contains the other metals as cyanides in combination with cyanide of potassium. The method of effecting their further separation will be learnt from what follows. In very accurate analyses bear in mind that the filtrate generally contains traces of bismuth, which may be precipitated by sulphide of ammonium. **147**

b. OXIDE OF SILVER FROM OXIDE OF MERCURY, OXIDE OF COPPER, AND OXIDE OF CADMIUM.

Add to the solution, which, if it contains much free acid, must previously be nearly neutralized with soda, cyanide of potassium until the precipitate which forms at first is redissolved. The solution contains the cyanides of the metals in combination with cyanide of potassium as soluble double salts. Add dilute nitric acid in excess, which effects the decomposition of the double cyanides; the insoluble cyanide of silver precipitates permanently, whilst the cyanide of mercury remains in solution, and the cyanides of copper and cadmium redissolve in the excess of nitric acid. Treat the cyanide of silver as directed § 115, 3. If the filtrate contains only mercury and cadmium, precipitate at once with sulphuretted hydrogen, which completely throws down the sulphides of the two metals; but if it contains copper, you must first heat with sulphuric acid, until the odor of hydrocyanic acid is no longer perceptible, and then precipitate with sulphuretted hydrogen (§ 119, 3). **148**

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* Pogg. Annal. 110, 432.

† Annal. d. Chem. u. Pharm. 43, 129.

c. OXIDE OF COPPER FROM OXIDE OF MERCURY, AND OXIDE OF CADMIUM.

Mix the solution, as in *b*, with cyanide of potassium until the precipitate which is first thrown down redissolves; add some more cyanide of potassium, then sulphuretted hydrogen water or sulphide of ammonium, as long as a precipitate forms. The sulphides of cadmium and mercury are completely thrown down, whilst the copper remains in solution, as sulphide dissolved in cyanide of potassium. Allow the precipitate to subside, decant repeatedly, treat the precipitate, for security, once more with solution of cyanide of potassium, heat gently, filter, and wash the sulphides of the metals. To determine the copper in the filtrate, evaporate the latter, with addition of nitric and sulphuric acids, until there is no longer any odor of hydrocyanic acid, and then precipitate with sulphuretted hydrogen (§ 119, 3). **149**

d. ALL THE METALS OF THE FIFTH GROUP FROM EACH OTHER.

Mix the dilute solution with carbonate of soda, then with cyanide of potassium in excess, digest some time at a gentle heat, and filter. On the filter you have carbonate of lead and of bismuth (containing alkali); separate the two metals by a suitable method. Add to the filtrate dilute nitric acid in excess, warm gently till the subcyanide of copper first precipitated with the cyanide of silver has redissolved, and filter off the undissolved silver salt, which is to be determined as directed § 115, 3. Neutralize the filtrate with carbonate of soda, add cyanide of potassium, and pass sulphuretted hydrogen in excess. Add now some more cyanide of potassium, to redissolve the sulphide of copper which may have fallen down, and filter the fluid, which contains the whole of the copper, from the precipitated sulphides of mercury and cadmium. Determine the copper as directed in *c*, and separate the mercury and cadmium as in **145** or **158**. **150**

4. *Methods based on the Formation and Separation of insoluble Basic Salts.*

a. TEROXIDE OF BISMUTH FROM OXIDES OF COPPER, CADMIUM, AND MERCURY (also from the oxides of the first four groups, with the exception of oxide of iron).

Precipitate the bismuth as basic chloride according to § 120, 4, and throw down the copper, &c. in the filtrate by sulphuretted hydrogen. Results thoroughly satisfactory (H. ROSE*.) **151**

b. TEROXIDE OF BISMUTH FROM OXIDES OF LEAD AND CADMIUM.

Separate the bismuth according to § 120, 1, *c*, as basic nitrate, and precipitate the lead and cadmium in the filtrate by sulphuretted hydrogen. Results very satisfactory (J. LÖWE†.) **152**

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* Pogg. Annal. 110, 430.

† Journ. f. prakt. Chem. 74, 345.

c. TEROXIDE OF BISMUTH AND OXIDE OF COPPER FROM OXIDES OF LEAD AND CADMIUM.

Separate the bismuth after § 120, 1, *c*, as basic nitrate, then heat the dish on the water-bath till the neutral nitrate of copper is completely converted into bluish-green basic salt and no blue solution is produced on addition of water. Allow to cool, treat with an aqueous solution of nitrate of ammonia (1 in 500), filter, wash with the same solution, and separate in the solution lead from cadmium; in the residue copper from bismuth. Results very satisfactory (J. LÖWE, *loc. cit.*).

5. *Methods based upon the Solubility of some of the Oxides in Ammonia, or Carbonate of Ammonia.*

a. OXIDE OF COPPER FROM TEROXIDE OF BISMUTH.

α. Mix the (nitric acid) solution with carbonate of ammonia in excess, and warm gently. The bismuth separates as carbonate, whilst the carbonate of copper is redissolved by the excess of carbonate of ammonia. As the precipitate, however, generally retains a little copper, it is necessary to redissolve it, after washing, in nitric acid, and precipitate again with carbonate of ammonia; the same operation must be repeated a third time if required. Some solution of carbonate of ammonia may be added to the water used for washing. Apply heat to the filtrate that the carbonate of ammonia may volatilize, acidify cautiously with hydrochloric acid, and determine the copper as subsulphide (§ 119, 3). The oxide of bismuth thus obtained is quite copper-free, but a little bismuth passes into the copper solution, hence the separation does not give such exact results as that in **151** (H. ROSE*). **153**

β. Mix the solution with some chloride of ammonium, and drop it gradually into dilute ammonia. The bismuth is precipitated as a basic salt, whilst the oxide of copper remains in solution as an ammoniacal double salt (BERZELIUS). Wash the precipitate with dilute ammonia, dissolve in dilute nitric acid, and determine as directed § 120. Determine the copper in the ammoniacal solution. In this method, also, it is advisable to precipitate twice, as in *α*.

b. OXIDE OF COPPER FROM OXIDE OF CADMIUM.

Add carbonate of ammonia in excess. Carbonate of cadmium separates, whilst the oxide of copper remains in solution with some oxide of cadmium. Upon exposure to air, the latter separates, the copper remaining in solution (STROMEYER). Treat the filtrate as in **153**. The process is more convenient than **149** or **159**, but the separation is less complete. **154**

c. CHLORIDE OF LEAD AND CHLORIDE OF SILVER may be separated also by solution of ammonia, which dissolves the latter, leaving the former behind as basic salt. Bear in mind that the chloride of silver must be recently precipitated, and with exclusion of light. The chloride of silver is thrown down from the ammoniacal solution by nitric acid. It is necessary to test the fluid filtered from the chloride of silver with sulphuretted hydrogen to ascertain whether weighable quantities of chloride of silver **155**

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[*] Pogg. Annal. 110, 430.

may not be retained in solution by the agency of the ammonia salts.

6. *Method based on the Precipitation of the Copper as Subsulphocyanide.*

OXIDE OF COPPER FROM OXIDE OF CADMIUM (and the oxides of Groups I.—IV. comp. 132).

Precipitate the copper according to § 119, 3, *b*, as subsulphocyanide (RIVOT), and the cadmium from the filtrate as sulphide. Results good (H. ROSE). Palladium may also be separated from copper in this way (WÖHLER*). 156

7. *Method based upon the different Deportment of the Chromates.*

BISMUTH FROM CADMIUM.

Precipitate the bismuth as directed § 120, 2. The filtrate contains the whole of the cadmium. Concentrate by evaporation, and then precipitate the cadmium by the cautious addition of carbonate of soda, as directed § 121, 1, *a* (J. LÖWE,† W. PEARSON‡). The results given are satisfactory. 157

8. *Method based upon the different Deportment of the Sulphides with Acids.*

a. OXIDE OF MERCURY FROM SILVER, BISMUTH, COPPER, CADMIUM, AND (but less well) FROM LEAD.

Boil the thoroughly washed precipitated sulphide with perfectly pure moderately dilute nitric acid. The sulphide of mercury is left undissolved, the other sulphides are dissolved. No chlorine may be present, and it is necessary that the sulphide of mercury should be pure, that is, free from finely divided mercury, which, as is well known, is precipitated when subsalts of mercury are treated with sulphuretted hydrogen. G. v. RATH§ employed this method, which is so universally used in qualitative analysis, with perfect success for the separation of mercury from bismuth. 158

b. OXIDE OF COPPER FROM OXIDE OF CADMIUM.

Boil the well-washed precipitate of the sulphides with dilute sulphuric acid (1 part concentrated acid and 5 parts water), and, after some time, filter the undissolved sulphide of copper, to be determined according to § 119, 3, from the solution containing the whole of the cadmium (A. W. HOFMANN‖). 159

9. *Methods based upon the Volatility of some of the Metals, Oxides, Chlorides, or Sulphides at a high Temperature.*

a. MERCURY FROM SILVER, LEAD, COPPER (in general from the metals forming non-volatile chlorides). 160

Precipitate with sulphuretted hydrogen, collect the precipitated sulphides on a weighed filter, dry at 100°, weigh, and mix uniformly. Introduce an aliquot part into the bulb *D* (fig. 106), pass a slow stream of chlorine gas, and apply a gentle heat to the bulb, increasing this gradually to faint redness. Connect *G* during the operation with a carboy containing moist hydrate of lime. First chloride of sulphur distils over, which decomposes with the water in *E* and *F* (p. 385); then the chloride of mercury formed volatilizes, condensing partly in *E*, partly in the hind part of *O*.

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* Annal. d. Chem. u. Pharm. 140, 144; Zeitschr. f. anal. Chem. 5, 403.

† Journ. f. prakt. Chem. 67, 469.

‡ Phil. Mag. 11, 204.

§ Pogg. Annal. 96, 322.

‖ Annal. d. Chem. u. Pharm. 115, 286.

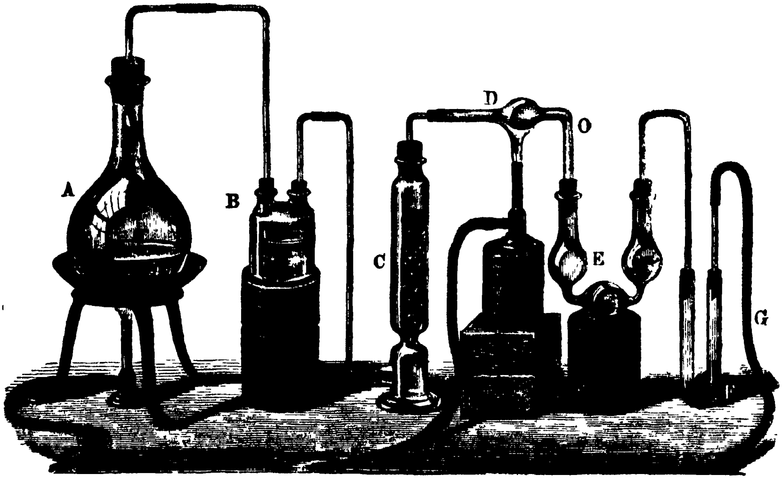

Fig. 106.

Cut off that part of the tube, rinse the sublimate with water into *E*, and mix the contents of the latter with the water in *F*. Mix the solution with excess of ammonia, warm gently till no more nitrogen is evolved, acidify with hydrochloric acid, and then determine in the fluid filtered from the sulphur which may still remain undissolved, the mercury as directed § 118, 3. If the residue consists of chloride of silver alone, or chloride of lead alone, you may weigh it at once; but if it contains several metals, you must reduce the chlorides by ignition in a stream of hydrogen, and dissolve the reduced metals in nitric acid, for their ulterior separation. Bear in mind that, in presence of lead, the sulphides and the chlorides must be heated *gently*, in the chlorine and hydrogen respectively, otherwise some chloride of lead might volatilize.

If it is intended to determine the mercury by the difference, instead of in the direct way, the apparatus may be much simplified. In this case, however, great care must be bestowed on the drying of the sulphides at 100°. Hence the method should only be adopted when a small quantity only of another metal is present with the mercury. Weigh the dried precipitate every half hour, and take the lowest weight as the correct one. Then ignite an aliquot part of the precipitate in the stream of hydrogen in a crucible with perforated cover, or in a tube with porcelain boat. The method cannot be applied unless only *one* metal is present with the mercury. From the residue in the crucible or boat reckon how much the whole precipitate, dried at 100°, would have yielded, then calculate the result into sulphide, in which form the substance was contained in the dried precipitate—the difference is sulphide of mercury. By ignition in hydrogen sulphide of silver yields the metal, sulphide of copper the subsulphide. In the presence of lead the last method is inapplicable, as sulphide of lead readily loses weight in a current of hydrogen (§ 83, *f*).

In alloys or mixtures of oxides the mercury may usually be determined with simplicity from the loss on ignition in the air or in hydrogen.

b. TEROXIDE OF BISMUTH FROM OXIDES OF SILVER, LEAD, AND COPPER.

161 The separation is effected exactly in the same way as that of mercury from the same metals (**160**). The method is more especially convenient for the separation of the metals in alloys. Care must be taken not to heat too strongly, as otherwise chloride of lead might volatilize; nor to discontinue the application of heat too soon, as otherwise bismuth would remain in the residue. AUG. VOGEL* gives 360° to 370° as the best temperature. Put water containing hydrochloric acid in *E* and *F* (fig. 106), and determine the bismuth therein according to § 120.

10. *Precipitation of one Metal in the Metallic State by another or the lower oxide of another.*

a. OXIDE OF LEAD FROM TEROXIDE OF BISMUTH.

162 Precipitate the solution with carbonate of ammonia (§ 116, 1, *a* and § 120, 1, *a*), wash the precipitated carbonates, and dissolve in acetic acid, in a flask; place a weighed rod of pure lead in the solution and nearly fill up with water, so that the rod may be entirely covered by the fluid; close the flask, and let it stand for about 12 hours, with occasional shaking. Wash the precipitated bismuth off from the lead rod, collect on a filter, wash, and dissolve in nitric acid; evaporate the solution, and determine the bismuth as directed § 120. Determine the lead in the filtrate as directed § 116. Dry the leaden rod, and weigh; subtract the loss of weight which the rod has suffered in the process, from the amount of the lead obtained from the filtrate (ULLGREN†). PATERA‡ recommends precipitating from dilute nitric solution, washing the precipitated bismuth first with water, then with alcohol, transferring to a small filter, drying and weighing. If it is feared that the finely divided bismuth has undergone oxidation, it is well to fuse it with cyanide of potassium (§ 120, 4).

b. SUBOXIDE OF COPPER FROM THE OXIDE.

163 Suboxide of copper may be determined with accuracy in presence of the oxide with the aid of a solution of nitrate of silver. The action of this salt upon suboxide of copper was first studied by H. ROSE.§ According to HAMPE,|| who further examined the

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* Zeitschr. f. anal. Chem. 13, 61.

† BERZELIUS' Jahresber. 21, 148.

‡ Zeitschr. f. anal. Chem. 5, 226.

§ Journ. f. prakt. Chem. 71, 412.

|| Zeitschr. f. anal. Chem. 13, 207.

matter with the greatest care, the action is as follows, sufficient dilution and a very gentle heat being implied: $3Cu_2O + 3(AgO, NO_5) + xHO = (4CuO, NO_5 + 3HO) + 2(CuO, NO_5) + 3Ag + (x-3) HO$. To the very finely divided mixture of the oxides add 200 times their amount of water, and an excess of perfectly pure neutral nitrate of silver, warm to 40°, allow to stand for three days, filter, wash, dissolve the precipitate in nitric acid, and estimate the silver therein as chloride. 3 eq. silver found correspond to 6 eq. copper present as suboxide. Determine in a second portion of the substance the total quantity of copper, and then find the quantity present as oxide by difference.

11. *Separation of Silver by Cupellation.*

CUPELLATION was formerly the universal method of determining SILVER in alloys with COPPER, LEAD, &c. The alloy is fused with a sufficient quantity of pure lead to give to 1 part of silver 16 to 20 parts of lead, and the fused mass is heated, in a muffle, in a small cupel made of compressed bone-ash. Lead and copper are oxidized, and the oxides absorbed by the cupel, the silver being left behind in a state of purity. One part by weight of the cupel absorbs the oxide of about 2 parts of lead; the quantity of the sample to be used in the experiment may be estimated accordingly. This method is only rarely employed in laboratories; I have given it a place here, however, because it is one of the safest processes to determine very small quantities of silver in alloys.* With regard to details, I refer to the "Determination of Silver in Galena," in the Special Part. 164

12. *Methods depending on the Volumetric Estimation of one oxide.*

a. SUBOXIDE OF COPPER IN PRESENCE OF THE OXIDE.†

Dissolve the substance, if necessary in a current of carbonic acid, in hydrochloric acid, and determine the chloride of copper in solution with protochloride of tin (§ 119, 4, *d*). In a second portion of the substance estimate the total quantity of copper according to one of the methods given § 119. 165

It results from the remarks on p. 261, that suboxide of copper in presence of oxide may also be estimated on the basis of the action of sesquichloride of iron upon the former.

b. OXIDE OF SILVER IN PRESENCE OF THE OXIDES OF LEAD AND COPPER.

Small quantities of silver may be estimated by PISANI'S method, § 115, II.

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* Compare MALAGUTI and DUROCHER, Compt. rend. 29, 689; DINGLER, 115, 276. Also W. HAMPE, Zeitschr. f. anal. Chem. 11, 221.

† The method of COMMAILLE (Compt. rend. 56, 309) can no longer be relied upon, since STAS has shown that the finely divided silver thrown down by ammoniacal solution of subchloride of copper dissolves largely in ammonia with access of air.

SIXTH GROUP.

TEROXIDE OF GOLD—BINOXIDE OF PLATINUM—PROTOXIDE OF TIN—BINOXIDE OF TIN—TEROXIDE OF ANTIMONY—(ANTIMONIC ACID)—ARSENIOUS ACID—ARSENIC ACID.

I. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM THE OXIDES OF THE FIRST FIVE GROUPS.

§ 164.

Index:—The Nos. refer to those in the margin.

Gold, from the oxides of Groups I.—III., 166, 171.
,, ,, IV., 166, 169, 171.
,, silver, 169, 188.
,, mercury, 169, 182.
,, lead, 169, 194.
,, copper, 169, 171.
,, bismuth, 169, 171, 194.
,, cadmium, 169, 171.
Platinum from the oxides of Groups I.—III., 166, 172.
,, ,, IV., 166, 170, 172.
,, silver, 170, 188.
,, mercury, 170, 172.
,, lead, 170.
,, copper, 170, 172.
,, bismuth, 170, 172.
,, cadmium, 170, 172.
Tin from the oxides of Groups I. and II., 166, 175, 181.
,, ,, III., 166, 175.
,, zinc, 166, 168, 173, 175.
,, manganese, 166, 168, 175.
,, nickel and cobalt, 166, 168, 173, 175, 180.
,, iron, 166, 168.
,, silver, 167, 168, 173, 180.
,, mercury, 167, 168, 173.
,, lead, 167, 168, 173, 180.
,, copper, 167, 168, 173, 175, 180.
,, bismuth, 167, 168.
,, cadmium, 167, 168, 173, 175.
Antimony from the oxides of Groups I. and II., 166, 178.
,, ,, III., 166.
,, zinc, 166, 168, 174.
,, manganese, 166, 168.
,, nickel and cobalt, 166, 168, 174, 179, 180.
,, iron, 166, 168, 178.
,, silver, 167, 168, 174, 180.
,, mercury, 167, 168, 174, 176, 189.
,, lead, 167, 168, 174, 180, 191.
,, copper, 167, 168, 174, 178, 180, 192.
,, bismuth, 167, 168.
,, cadmium, 167, 168, 174.
Arsenic from oxides of Group I., 166, 178, 184, 186, 187.
,, ,, II., 166, 177, 178, 184, 186, 187, 190.
,, ,, III., 166, 185, 186.
,, zinc, 166, 168, 177, 183, 184, 186, 187.
,, manganese, 166, 168, 177, 183, 185, 186, 187.
,, nickel and cobalt, 166, 168, 177, 179, 180, 183, 184, 185, 186, 187.
,, iron, 166, 168, 177, 178, 183, 185, 186.
,, silver, 167, 168, 177, 180, 186.
,, mercury, 167, 168, 186, 189.
,, lead, 167, 168, 177, 180, 183, 184, 186, 190.
,, copper, 167, 168, 177, 178, 180, 183, 184, 185, 186, 192, 193.
,, bismuth, 167, 168, 177, 186.
,, cadmium, 167, 168, 177, 184, 185, 186.

A. *General Methods.*

1. *Method based upon the Precipitation of Oxides of the Sixth Group from Acid Solutions by Sulphuretted Hydrogen.*

ALL OXIDES OF THE SIXTH GROUP FROM THOSE OF THE FIRST FOUR GROUPS.

Conduct into the acid* solution sulphuretted hydrogen in excess, and filter off the precipitated sulphides (corresponding to the oxides of the sixth group). **166**

The points mentioned **127**, *a*, *β*, and *γ* must also be attended to here. As regards *γ*, antimony and tin are to be inserted between cadmium and mercury, in the order of metals there given. With respect to the particular conditions required to secure the proper precipitation of certain metals of the sixth group, I refer to Section IV. I have to remark in addition :—

a. That sulphuretted hydrogen fails to separate arsenic acid from oxide of zinc, as, even in presence of a large excess of acid, the whole or at least a portion of the zinc precipitates with the arsenic (WÖHLER). To secure the separation of the two bodies in a solution, the arsenic acid must first be converted into arsenious acid, by heating with sulphurous acid, before the sulphuretted hydrogen is conducted into the fluid.

β. That in presence of antimony, tartaric acid should be added, as otherwise the sulphide of antimony will contain chloride; and that sulphide of antimony, when thrown down from a boiling solution by sulphuretted hydrogen, becomes black after a time and so dense that it is deposited like sand, whereby the filtration and washing are much facilitated (S. P. SCHÄFFELER†).

2. *Method based upon the Solubility of the Sulphides of the Metals of the Sixth Group in Sulphides of the Alkali Metals.*

a. THE OXIDES OF GROUP VI. (with the exception of Gold and Platinum) FROM THOSE OF GROUP V. **167**

Precipitate the acid solution with sulphuretted hydrogen, paying due attention to the directions given in Section IV. under the heads of the several metals, and also to the remarks in **166**. The precipitate consists of the sulphides of the metals of Groups V. and VI. Wash, and treat at once with yellow sulphide of ammonium in excess. (It is usually best to spread out the filter in a porcelain dish, add the sulphide of ammonium, cover with a large watch glass, and place on a heated water-bath. Unnecessary exposure to air should be avoided.) Add some water, filter off the clear fluid, treat the residue again with sulphide of ammonium, digest a short time, repeat the same operation, if necessary, a third and fourth time, filter, and wash the residuary sulphides of Group V. with water containing sulphide of ammonium. If protosulphide of tin is present, some flowers of sulphur must be added to the sulphide of ammonium, unless the latter be very yellow. In presence of copper, the sulphide of which is a little soluble in sulphide of ammonium, sulphide of sodium should be used instead.

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* Hydrochloric acid answers best as acidifying agent.

† Berichte der deutschen chem. Gesellsch. 1871, 279. I have myself confirmed these observations.

However, this substitution can be made only in the absence of mercury, since the sulphide of that metal is soluble in sulphide of sodium.

Add to the alkaline filtrate, gradually, hydrochloric acid in small portions, until the acid predominates; allow to subside, and then filter off the sulphides of the metals of the sixth group, which are mixed with sulphur.

SCHNEIDER* states that he failed in effecting complete separation of bisulphide of bismuth from bisulphide of tin by digestion with sulphide of potassium, but succeeded by conducting sulphuretted hydrogen into the potassa solution of tartrate of teroxide of bismuth and protoxide of tin (which decompose into binoxide of bismuth and binoxide of tin).

If a solution contains much arsenic acid in presence of small quantities of copper, bismuth, &c., it is convenient to precipitate these metals (together with a very small amount of sulphide of arsenic) by a brief treatment with sulphuretted hydrogen. Filter, extract the precipitate with sulphide of ammonium (or sulphide of potassium), acidify the solution obtained, mix it with the former filtrate containing the principal quantity of the arsenic, and proceed to treat further with sulphuretted hydrogen (§ 127, 4, *b*).

b. THE OXIDES OF GROUP VI. (with the exception of Gold and Platinum) FROM THOSE OF GROUPS IV. AND V. **168**

a. Neutralize the solution with ammonia, add chloride of ammonium, if necessary, and then yellow sulphide of ammonium in excess; digest in a closed flask, for some time at a moderate heat, and then proceed as in **167**. Repeated digestion with fresh quantities of sulphide of ammonium is indispensable. On the filter, you have the sulphides of the metals of Groups IV. and V. Wash with water containing sulphide of ammonium. In presence of nickel, this method offers peculiar difficulties; traces of sulphide of mercury, too, are liable to pass into the filtrate. In presence of copper (and absence of mercury), soda and sulphide of sodium are substituted for ammonia and sulphide of ammonium.†

β. In the analysis of solid compounds (oxides or salts), it is in most cases preferable to fuse the substance with 3 parts of dry carbonate of soda and 3 of sulphur, in a covered porcelain crucible. When the contents are completely fused, and the excess of sulphur is volatilized, the mass is allowed to cool, and then treated with water, which dissolves the sulphosalts of the metals of the sixth group, leaving the sulphides of Groups IV. and V. undissolved. By this means, even ignited binoxide of tin may be readily tested for iron, &c., and the amount of the admixture determined (H. ROSE).

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* Annal. d. Chem. u. Pharm. 101, 64.

† The accuracy of this method has been called in question by BLOXAM (Quart. Journ. Chem. Soc. 5, 119). That chemist found that sulphide of ammonium fails to separate small quantities of bisulphide of tin from large quantities of sulphide of mercury or sulphide of cadmium (1 : 100); and that more especially the separation of copper from tin and antimony (also from arsenic) by this method is a failure, as nearly the whole of the tin remains with the copper. The latter statement I cannot confirm, for MR. LUCIUS, in my laboratory, has succeeded in separating copper from tin by means of yellowish sulphide of sodium completely; but it is indispensable to digest three or four times with sufficiently large quantities of the solvent, as stated in the text.

B. *Special Methods.*

1. *Methods based upon the Insolubility of some Metals of the Sixth Group in Acids.*

a. GOLD FROM METALS OF GROUPS IV. AND V. IN ALLOYS.

α. Boil the alloy with pure nitric acid (not too concentrated), 169
or, according to circumstances, with hydrochloric acid. The other metals dissolve, the gold is left. The alloy must be reduced to filings, or rolled out into a thin sheet. If the alloy were treated with concentrated nitric acid, and at a temperature below boiling, a little gold might dissolve in consequence of the co-operation of nitrous acid. In the presence of silver and lead, this method is only applicable when they amount to more than 80 per cent., since otherwise they are not completely dissolved. Alloys of silver and gold containing less than 80 per cent. of silver are therefore fused with 3 parts of lead, before they are treated with nitric acid. The residuary gold is weighed; but its purity must be ascertained, by dissolving in cold dilute nitrohydrochloric acid, not in concentrated hot acid, as chloride of silver also is soluble in the latter. In the presence of silver a small quantity of its chloride is usually obtained here. If it can be weighed, it should be reduced and deducted.

At the Mint Conference held at Vienna in 1857, the following process was agreed upon for the mints in the several states of Germany. Add to 1 part of gold, supposed to be present, 2½ parts of pure silver; wrap both the alloy and the silver in paper together, and introduce into a cupel in which the requisite amount of lead is just fusing.[†] After the lead has been absorbed,[‡] the button is flattened by hammering or rolling, then ignited and rolled. The rolls are treated first with nitric acid of 1·2 sp. gr., afterwards with nitric acid of 1·3 sp. gr., rinsed, ignited, and weighed.[§] Even after boiling again with nitric acid of 1·3 sp. gr., they retain ·75 to 1-thousandth of silver which will remain as chloride if the rolls are treated with cold dilute aqua regia (H. Rössler, *loc. cit.*).

β. Heat the alloy (previously filed or rolled) in a capacious pla-

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[*] Zeitschr. f. anal. Chem. 5, 405.

[†] If the weighed sample, say ·25 grm., contains 98–92% gold, 3 grm. of lead are required; if 92–87·5, 4 grm.; if 87·5–75, 5 grm.; if 75–60, 6 grm.; if 60–35, 7 grm.; if less than 35, 8 grm.

[‡] A small quantity of gold—from one to three thousandths—is always lost in cupellation. The loss increases with the amount of lead, and is also dependent on the proportion of silver to gold. The more silver present the less is the loss of gold. In large buttons the loss is less than in small ones (H. Rössler, Ding. polyt. Journ. 206, 185; Zeitschr. f. anal. Chem. 13, 87).

[§] Kunst- und Gewerbeblatt f. Baiern, 1857, 151; Chem. Centralbl. 1857, 307; Polyt. Centralbl 1857, 1151, 1471, 1639.

tinum dish with a mixture of 2 parts pure concentrated sulphuric acid and 1 part water, until the evolution of gas has ceased, and the sulphuric acid begins to volatilize; or fuse the alloy with bisulphate of potassa (H. ROSE). Separate the gold from the sulphates of the other metals, by treating the mass with water which should finally be boiling. It is advisable to repeat the operation with the separated gold, and ultimately test the purity of the latter. In presence of lead this method is not good.

γ. The methods given in *a* and *β* may be united, *i.e.*, the cupelled and thinly-rolled metal may be first warmed with nitric acid of 1·2 sp. gr., then thoroughly washed, the gold boiled 5 minutes with concentrated sulphuric acid, washed again, and ignited (MASCAZZINI, BUGATTI).

b. PLATINUM FROM METALS OF GROUPS IV. AND V., IN ALLOYS.

170 The separation is effected by heating the alloy in filings or foil with pure concentrated sulphuric acid, with addition of a little water, or by fusing with bisulphate of potash (**169**, *β*); but not with nitric acid, as platinum in alloys will, under certain circumstances, dissolve in that acid.

2. *Method based upon the Separation of Gold in the metallic state.*

GOLD FROM ALL OXIDES OF GROUPS I.—V., with the exception of OXIDE OF LEAD, SUBOXIDE OF MERCURY, AND OXIDE OF SILVER.

171 Precipitate the hydrochloric acid solution with oxalic acid as directed § 123, *b*, *γ*, or with sulphate of iron, § 123, *b*, *a*, and filter off the gold when it has completely separated. Take care to add a sufficient quantity of hydrochloric acid after the reduction to insure solution of any oxalates. In the presence of copper the addition of hydrochloric acid does not suffice, since the coprecipitated oxalate of copper will dissolve with difficulty in this acid. E. PUROOTTI* recommends in this case, after precipitation, adding potash cautiously to the boiling hot fluid till it is neutral, and then if necessary some neutral oxalate of potash. Double oxalate of copper and potash will be formed which dissolves with a blue color. The gold after washing will now be pure.

3. *Method based upon the Precipitation of Platinum as Potassio- or Ammonio-bichloride of Platinum.*

PLATINUM FROM THE OXIDES OF GROUPS IV. AND V., with the exception of SUBOXIDE OF MERCURY, OXIDE OF LEAD, AND OXIDE OF SILVER.

172 Precipitate the platinum with chloride of potassium or chloride of ammonium as directed § 124, and wash the precipitate thoroughly with spirit of wine. The platinum prepared from the precipitated ammonium or potassium salt is to be tested after being weighed, to see whether it yields any metal (especially iron) to fusing bisulphate of potassa.

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* Zeitschr. f. anal. Chem. 9, 128.

4. *Methods based upon the Separation of Oxides insoluble in Nitric Acid.*

a. TIN FROM METALS OF GROUPS IV. AND V. (not from Bismuth, Iron, or Manganese*) IN ALLOYS.

Treat the finely divided alloy, or the metallic powder obtained 173 by reducing the oxides in a stream of hydrogen with nitric acid, as directed § 126, 1, *a*. The filtrate contains the other metals as nitrates. As binoxide of tin is liable to retain traces of copper and lead and iron, you must, in an accurate analysis, test an aliquot part of it for these bodies, and determine their amount as directed **168**, *β*.

BRUNNER recommends the following course of proceeding, by which the presence of copper in the tin may be effectually guarded against. Dissolve the alloy in a mixture of 1 part of nitric acid, 4 parts of hydrochloric acid, and 5 parts of water; dilute the solution largely with water, and heat gently. Add crystals of carbonate of soda until a distinct precipitate has formed, and boil. (In presence of copper, the precipitate must, in this operation, change from its original bluish-green to a brown or black tint.) When the fluid has been in ebullition some 10 or 15 minutes, allow it to cool, and then add nitric acid, drop by drop, until the reaction is distinctly acid; digest the precipitate for several hours, when it should have acquired a pure white color. The binoxide of tin thus obtained is free from copper; but it may contain some iron, which can be removed as directed in **168**, *β*.

Before the binoxide of tin can be considered pure, it must be tested also for silicic acid, as it frequently contains traces of this substance. To this end, an aliquot part is fused in platinum with 3—4 parts of carbonate of soda and potassa, the fused mass boiled with water, and the solution filtered; hydrochloric acid is then added to the filtrate, and, should silicic acid separate, the fluid is filtered off from this substance. The tin is then precipitated by sulphuretted hydrogen, and the silicic acid still remaining in the filtrate is determined in the usual way (§ 140). If hydrochloric acid has produced a precipitate of silicic acid, the last filtration is effected on the same filter (KHITTEL†).

b. ANTIMONY FROM THE METALS OF GROUPS IV. AND V. IN ALLOYS (not from bismuth, iron, and manganese).

Proceed as in **173**, filter off the precipitate, and convert it by 174 *ignition into antimoniate of teroxide of antimony* (§ 125, 2). Results only approximative, as a little teroxide of antimony dissolves. Alloys of antimony and lead, containing the former metal in excess, should be previously fused with a weighed quantity of pure lead (VARRENTRAPP‡).

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* If the alloy of tin contains bismuth or manganese, there remains with the binoxide of tin always teroxide of bismuth or sesquioxide of manganese, which cannot be extracted by nitric acid; if it contains iron, on the contrary, some binoxide of tin always dissolves with the iron, and cannot be separated even by repeated evaporation (H. ROSE, Pogg. Annal. 112, 169, 170, 172).

† Chem. Centralbl. 1857, 929.

‡ Dingler's polyt. Journ. 158, 316.

5. *Methods based on the Precipitation of Binoxide of Tin by Neutral Salts* (e.g., *Sulphate of Soda*) *or by Sulphuric Acid.*

TIN FROM THE OXIDES OF GROUPS I., II., III.; ALSO FROM PROTOXIDE OF MANGANESE, OXIDE OF ZINC, PROTOXIDES OF NICKEL AND COBALT, OXIDE OF COPPER, OXIDE OF CADMIUM (TEROXIDE OF GOLD).

Precipitate the hydrochloric acid solution, which must contain the tin entirely as binoxide (bichloride), according to § 126, 1, *b*, by nitrate of ammonia or sulphate of soda (LÖWENTHAL), or by sulphuric acid, which, H. ROSE says, answers equally well. Alloys are always treated as follows:—First, oxidize by digestion with nitric acid; when no more action takes place, evaporate the greater portion of the nitric acid in a porcelain dish, moisten the mass with strong hydrochloric acid, and after half an hour add water, in which the metachloride of tin and the other chlorides dissolve. Alloys of tin and gold are dissolved in aqua regia, the excess of acid evaporated, and the solution diluted with much water, before precipitating with sulphuric acid. **175**

It must be remembered that in this process any phosphoric acid that may be present is precipitated entirely or partially with the binoxide of tin. After the precipitate has been well washed by decantation, LÖWENTHAL recommends to boil with a mixture of 1 part nitric acid (sp. gr. 1·2) and 9 parts water, then to transfer to the filter, and wash thoroughly. Results very satisfactory. If the fluid contains sesquioxide of iron, a portion of the latter always falls down with the tin. Hence the binoxide of tin must be tested for iron according to **168**, *β*, which, if present, must be determined and deducted.

6. *Method based on the Insolubility of Sulphide of Mercury in Hydrochloric Acid.*

MERCURY FROM ANTIMONY.

Digest the precipitated sulphides with moderately strong hydrochloric acid in a distilling apparatus. The sulphide of antimony dissolves, while the sulphide of mercury remains behind. Expel all the hydrosulphuric acid, then add tartaric acid, dilute, filter, mix the filtrate with the distillate which contains a little antimony, and precipitate with sulphuretted hydrogen. The sulphide of mercury may be weighed as such (F. FIELD*). **176**

7. *Methods based upon the Conversion of Arsenic and Antimony into Alkaline Arseniate and Antimoniate.*

a. ARSENIC FROM THE METALS AND OXIDES OF GROUPS II., IV., AND V.

If you have to do with arsenites or arseniates, fuse with 3 parts of carbonate of soda and potassa and 1 part of nitrate of potassa; if an alloy has to be analysed it is fused with 3 parts of carbonate of soda and 3 parts of nitrate of potassa. In either case the residue is boiled with water, and the solution, which contains the arseniates of the alkalies, filtered from the undissolved oxides or **177** carbonates. The arsenic acid is determined in the filtrate as directed § 127, 2. If the quantity of arsenic is only small, a platinum crucible may be used, otherwise a porcelain crucible must be used, as platinum would be seriously injured. In the latter case, bear in mind that the fused mass is contaminated with silicic acid and alumina. If the alloy contains much arsenic a small quantity may be readily lost by volatilization, even though the operation be cautiously conducted. In such a case, therefore, it is better first to oxidize with nitric acid, then to evaporate, and to fuse the residue as above directed with carbonate of soda and nitrate of potassa.

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* Quart. Journ. Chem. Soc. 12, 32.

b. ARSENIC AND ANTIMONY FROM COPPER AND IRON, especially in ores containing sulphur.

Diffuse the very finely pulverized mineral through pure solution of potassa, and conduct chlorine into the fluid (comp. p. 388). The iron and copper separate as oxides, the solution contains sulphate, arseniate, and antimoniate of potassa (RIVOT, BEUDANT, and DAGUIN*). **178**

c. ARSENIC AND ANTIMONY FROM COBALT AND NICKEL.

Dilute the nitric acid solution, add a large excess of potassa, heat gently, and conduct chlorine into the fluid until the precipitate is black. The solution contains the whole of the arsenic and antimony, the precipitate the nickel and cobalt as sesquioxides (RIVOT, BEUDANT, and DAGUIN, *loc. cit.*). **179**

8. *Methods based upon the Volatility of certain Chlorides or Metals.*

a. TIN, ANTIMONY, ARSENIC FROM COPPER, SILVER, LEAD, COBALT, NICKEL.

Treat the sulphides with a stream of perfectly dry chlorine, proceeding exactly as directed in **160**. In presence of antimony, fill the tubes *E* and *F* (fig. 106) with a solution of tartaric acid in water, mixed with hydrochloric acid. The metals may be also separated by this method in alloys. The alloy must be very finely divided. Arsenical alloys are only very slowly decomposed in this way. In separating arsenic and copper the temperature must not exceed 200°, and chlorine water should be put into the receiver (PARNELL†). If tin and copper are separated in this manner, according to the experience of H. ROSE,‡ a small trace of tin remains with the chloride of copper. **180**

b. BINOXIDE OF TIN, TEROXIDE OF ANTIMONY (AND ALSO ANTIMONIC ACID), ARSENIOUS, AND ARSENIC ACIDS, FROM ALKALIES AND ALKALINE EARTHS.

Mix the solid compound with 5 parts of pure chloride of ammonium in powder, in a porcelain crucible, cover this with a concave platinum lid, on which some chloride of ammonium is sprinkled, and ignite gently until all chloride of ammonium is driven off; mix the contents of the crucible with a fresh portion **181** of that salt, and repeat the operation until the weight remains constant. In this process, the chlorides of tin, antimony, and arsenic escape, leaving the chlorides of the alkaline and alkaline earthy metals. The decomposition proceeds most rapidly with alkaline salts. With regard to alkaline earthy salts it is to be observed that those which contain antimonic acid or binoxide of tin are generally decomposed completely by a double ignition with chloride of ammonium (magnesia alone cannot be separated perfectly from antimonic acid by this method). The alkaline earthy arseniates are the most troublesome; the baryta, strontia, and lime salts usually require to be subjected 5 times to the operation, before they are free from arsenic, and the arseniate of magnesia it is impossible thoroughly to decompose in this way (H. ROSE*). According to SALKOWSKI† arseniate of baryta may be converted into chloride quite free from arsenic by one ignition with chloride of ammonium; however arsenate of lime was found to leave a residue containing arsenic acid even after six ignitions with chloride of ammonium.

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* Compt. rend. 1853, 835; Journ. f. prakt. Chem. 61, 133.

† Chem. News, 21, 133.

‡ Pogg. Annal. 112, 169.

c. MERCURY FROM GOLD (SILVER, AND GENERALLY FROM THE NON-VOLATILE METALS).

Heat the weighed alloy in a porcelain crucible, ignite till the weight is constant, and determine the mercury from the loss. If it is desired to estimate it directly, the apparatus, fig. 84, p. 250, may be used. In cases where the separation of mercury from metals that oxidize on ignition in the air is to be effected by this method, the operation must be conducted in an atmosphere of hydrogen (p. 200, fig. 79). **182**

9. *Methods based on the Volatility of Sulphide of Arsenic.*

ARSENIC ACID FROM THE OXIDES OF MANGANESE, IRON, ZINC, COPPER, NICKEL, COBALT (NOT SO WELL FROM OXIDE OF LEAD, AND NOT FROM OXIDES OF SILVER, ALUMINUM, OR MAGNESIUM).

Mix the arsenic acid compound (no matter whether it has been air-dried or gently ignited) with sulphur, and ignite under a good draught in an atmosphere of hydrogen (p. 200, fig. 79; the perforated lid must in this case be of porcelain; platinum would not answer). The whole of the arsenic volatilizes, the sulphides of manganese, iron, zinc, lead, and copper remains behind; they may be weighed directly. After weighing, add a fresh quantity of sulphur to the residue, ignite as before, and weigh again; repeat this operation until the weight remains constant. Usually, if the compound was intimately mixed with the sulphur, the conversion of the arsenate into sulphide is complete after the first ignition. Results very good. **183**

In separating *nickel* the analyst will remember that the residue cannot be weighed directly, since it does not possess a constant composition; hence the ignition in hydrogen may be saved; arsenate of nickel loses all its arsenic on being simply mixed with sulphur and heated. The heat should be moderate and continued till no more red sulphide of arsenic is visible on the inside of the porcelain crucible. It is advisable to repeat the operation. The separation of arsenic from *cobalt* cannot be completely effected in this manner even by repeated treatment with sulphur, but it can be effected by oxidizing the residue with nitric acid, evaporating to dryness, mixing with sulphur, and reigniting. Smaltine and cobaltine must be treated in the same manner (H. Rose*). I should not forget to mention that Ebelmen,† a long while ago, noticed the separation of arsenic acid from sesquioxide of iron by ignition in a stream of sulphuretted hydrogen.

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* Pogg. Annal. 73, 582; 74, 578; 112, 173.

† Journ. f. prakt. Chem. 104, 138.

10. *Method based upon the Separation of Arsenic as Arsenate of Suboxide of Mercury.*

Arsenic Acid from the Alkalies, Alkaline Earths, Oxide of Zinc, Protoxide of Cobalt, Protoxide of Nickel, Oxide of Lead, Oxide of Copper, Oxide of Cadmium.

Proceed exactly as in the separation of phosphoric acid by mercury (§ 134, *b*, γ). The arsenic acid *cannot* be determined in the insoluble residue in the way in which the phosphoric acid is determined. If it is desired to estimate it directly, one of the methods given in this § must be used to separate it from the suboxide of mercury. Treat the filtrate as directed § 135, *k*, *a* (H. Rose.) 184

11. *Method based upon the Separation of Arsenic as Arsenate of Magnesia and Ammonia.*

Arsenic Acid from Oxide of Copper, Oxide of Cadmium, Sesquioxide of Iron, Protoxide of Manganese, Protoxide of Nickel, Protoxide of Cobalt, Alumina.

Mix the hydrochloric acid solution, which must contain the whole of the arsenic in the form of arsenic acid, with enough tartaric acid to prevent precipitation by ammonia, precipitate the arsenic acid according to § 127, 2, as arseniate of magnesia and ammonia, allow to settle, filter, wash once with a mixture of 3 parts water and 1 part ammonia, redissolve in hydrochloric acid, add a very minute quantity of tartaric acid, supersaturate again with ammonia, add some more chloride of magnesium and ammonium, allow to deposit, and determine the now pure precipitate according to § 127, 2. In the filtrate the bases of Groups IV. and V. may be precipitated by sulphide of ammonium; if alumina is present, evaporate the filtrate from the sulphides with addition of carbonate of soda and a little nitre to dryness, fuse, and estimate the alumina in the residue. The method is more adapted to the separation of rather large than of very small quantities of arsenic from the above named oxides, since in the case of small quantities the minute portions of arseniate of magnesia and ammonia that remain in solution may exercise a considerable influence on the accuracy of the result. 185

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* Zeitschr. f. anal. Chem. 1, 413.

† Annal. de Chim. et de Phys. (3) 25, 98.

12. *Method based upon the Separation of Arsenic as Arseniomolybdate of Ammonia.*

ARSENIC ACID FROM ALL OXIDES OF GROUPS I.—V.

Separate the arsenic acid as directed in § 127, 2, *b*; long continued heating at 100° is indispensable. The determination of the bases is most conveniently effected in a special portion. **186**

13. *Method based upon the Insolubility of Arseniate of Sesquioxide of Iron.*

ARSENIC ACID FROM THE BASES OF GROUPS I. AND II., AND FROM OXIDE OF ZINC, AND THE PROTOXIDES OF MANGANESE, NICKEL, AND COBALT.

Mix the hydrochloric solution with a sufficient quantity of pure sesquichloride of iron, neutralize the greater part of the free acid with carbonate of soda, and precipitate the iron and arsenic acid together with carbonate of baryta in the cold or with acetate of soda at a boiling heat. The precipitate should be so basic as to have a brownish-red color. The method is especially suitable for the separation of arsenic acid when its estimation is not required. However the precipitate may be dissolved in hydrochloric acid and the arsenic estimated by precipitation with sulphuretted hydrogen. **187**

14. *Methods based upon the Insolubility of some Chlorides.*

a. SILVER FROM GOLD.

Treat the alloy with cold dilute nitrohydrochloric acid, dilute, and filter the solution of the terchloride of gold from the undissolved chloride of silver. This method is applicable only if the alloy contains less than 15 per cent. of silver; for if it contains a larger proportion, the chloride of silver which forms protects the undecomposed part from the action of the acid. In the same way silver may be separated also from *platinum.* **188**

b. OXIDE OF MERCURY FROM THE OXYGEN COMPOUNDS OF ARSENIC AND ANTIMONY.

Precipitate the mercury from the hydrochloric solution by means of phosphorous acid as subchloride (§ 118, 2). The tartaric acid, which in the presence of antimony must be added, does not interfere with the reaction (H. ROSE*). **189**

15. *Methods based upon the Insolubility of certain Sulphates in Water or Spirit of Wine.*

a. ARSENIC ACID FROM BARYTA, STRONTIA, LIME, AND OXIDE OF LEAD.

Proceed as for the separation of phosphoric acid from the same oxides (§ 135, *b*). The compounds of these bases with arsenious acid are first converted into arsenates, before the sulphuric acid is added; this conversion is effected by heating the hydrochloric acid solution with chlorate of potassa or by means of bromine. **190**

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* Pogg. Annal. 110, 536.

b. ANTIMONY FROM LEAD.

Treat the alloy with a mixture of nitric and tartaric acids. **191** The solution of both metals takes place rapidly and with ease. Precipitate the greater part of the lead as sulphate (§ 116, 3), filter, precipitate with sulphuretted hydrogen, and treat the sulphides according to **168**, with sulphide of ammonium, in order to separate the antimony from the lead left unprecipitated by the sulphuric acid (A. STRENG*).

16. *Method based upon the Separation of Copper as Subsulphocyanide or Subiodide.*

COPPER FROM ARSENIC AND ANTIMONY.

From the properly prepared solution precipitate the copper by **192** § 119, 3, *b*, as subsulphocyanide, allow to settle, filter, wash with water containing nitrate of ammonia (to prevent the washings being muddy), and estimate antimony and arsenic in the filtrate, precipitating first with sulphuretted hydrogen. Results good. The following method, which depends on precipitating the copper as subiodide, is not so good: Dissolve in nitric or sulphuric acid, taking care to add the acid only slightly in excess, dilute (in presence of antimony, with water containing tartaric acid) and precipitate the copper with sulphurous acid and iodide of potassium. Arsenic and antimony remain in solution (FLAJOLOT). Results approximate, since a little subiodide of copper remains in solution by the agency of the excess of sulphurous acid. Reduction of the copper by protochloride of tin, as FLEISCHER† recommends, is impracticable in this case, as the separation of tin from arsenic and antimony would be too difficult.

17. *Method based upon the Separation of Copper as Oxalate.*

COPPER FROM ARSENIC.

Add to the nitric acid solution ammonia until the blue precipitate formed remains undissolved, then effect solution by an **193** excess of oxalate of ammonia. Add, cautiously, hydrochloric or nitric acid to acid reaction, and allow the mixture to stand. The copper separates almost completely as oxalate, which is then converted by ignition in the air into oxide. Add ammonia to the filtrate, and precipitate with a few drops of sulphide of ammonium the minute trace of copper still retained in solution (F. FIELD‡).

18. *Method based upon the different Deportment with Cyanide of Potassium.*

GOLD FROM LEAD AND BISMUTH.

These metals may be separated in solution by cyanide of **194** potassium in the same way in which the separation of mercury from lead and bismuth is effected (see **147**). The solution of the double cyanide of gold and potassium is decomposed by boiling with aqua regia, and, after expulsion of the hydrocyanic acid, the gold determined by one of the methods given in § 123.

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* Ding. polyt. Journ. 151, 389

† Zeitschr. f. anal. Chem. 9, 256.

‡ Chem. Gaz. 1857, 313.

II. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM EACH OTHER.

§ 165.

Index:—The Nos. refer to those in the margin.
Platinum from gold, 195, 214, 215.
,, tin, antimony, and arsenic, 196.
Gold from platinum, 195, 214, 215.
,, tin, 196, 213.
,, antimony and arsenic, 196.
Tin from platinum, 196.
,, gold, 175, 196, 213.
,, arsenic, 199, 206, 207, 208, 211, 212, 216, 217.
,, antimony, 197, 201, 208, 209, 210, 212, 216.
Protoxide of tin from the binoxide, 221.
Antimony from platinum and gold, 196.
,, arsenic, 200, 201, 202, 203, 204, 206, 207.
,, tin, 197, 201, 208, 209, 210, 212, 216.
Teroxide of antimony from antimonic acid, 220.
Arsenic from platinum and gold, 196.
,, tin, 199, 206, 207, 208, 211 212, 216, 217.
,, antimony, 200, 201, 202, 203, 204, 206, 207, 218.
Arsenious acid from arsenic acid, 198, 205, 219.

1. *Method based upon the Precipitation of Platinum as Potassio-bichloride of Platinum.*

PLATINUM FROM GOLD.

Precipitate from the solution of the chlorides the platinum as directed § 124, *b*, and determine the gold in the filtrate as directed § 123, *b*. **195**

2. *Methods based upon the Volatility of the Chlorides of the inferior Metals.*

a. PLATINUM AND GOLD FROM TIN, ANTIMONY, AND ARSENIC.

Heat the finely divided alloy or the sulphides in a stream of chlorine gas. Gold and platinum are left, the chlorides of the other metals volatilize (compare **160**). **196**

b. ANTIMONY FROM TIN.

The tin should be present wholly as protochloride or protoxide. Precipitate with sulphuretted hydrogen, filter (preferably through an asbestos filtering tube), dry the precipitate, and pass through it a current of dry hydrochloric gas at the ordinary temperature. The sulphides are converted into the corresponding chlorides; the chloride of antimony alone escapes, and may be received in water. Dissolve the residual protochloride of tin in water containing hydrochloric acid, and estimate the tin according to § 126 (C. TOOKEY*). The method can only be used in rare cases, as it is difficult to obtain a precipitate quite free from bisulphide of tin. **197**

c. ARSENIOUS ACID FROM ARSENIC ACID.

The amount of substance taken should not contain more than ·2 grm. arsenious acid. Heat with 45 grm. chloride of sodium, **198**

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* Journ. Chem. Soc. 15, 462.

135 grm. sulphuric acid (free from arsenic) of 1·61 sp. gr., and 30 grm. water in a tubulated retort containing a spiral of platinum, and provided with a thermometer. The temperature should rise to about 125°. Determine the arsenic in the distillate according to § 127, 4, *a*, in the residue according to § 127, 4, *b*. The sulphide obtained from the former corresponds to the arsenious acid, from the latter to the arsenic acid. Results satisfactory (RIECKHER*.) If the substance given is a dilute fluid, render slightly alkaline with carbonate of soda, and concentrate to about 20 c.c., finally in a tubulated retort. I can recommend the apparatus fig. 78, p. 179. At the exit of the U-tube it is well to attach a tube with a bulb (a chloride of calcium tube) containing fragments of glass, moistened with weak soda solution, to prevent all chance of chloride of arsenic escaping; in the receivers water is placed. At the end of the operation rinse the chloride of calcium tube, and mix with the contents of the receiver.

3. *Methods based upon the Volatility of Arsenic and Tersulphide of Arsenic.*

a. ARSENIC FROM TIN (H. ROSE).

Convert into sulphides or oxides, dry at 100°, and heat a weighed **199** portion with addition of a little sulphur in a bulb-tube, gently at first, but gradually more strongly, conducting a stream of dry sulphuretted hydrogen gas through the tube during the operation. Sulphur and sulphide of arsenic volatilize, sulphide of tin is left. The sulphide of arsenic is received in U-tubes containing dilute ammonia, which are connected with the bulb-tube in the manner described in **160**. When upon continued application of heat no sign of further sublimation is observed in the colder part of the bulb-tube, drive off the sublimate which has collected in the bulb, allow the tube to cool, and then cut it off above the coating. Divide the separated portion of the tube into pieces, and heat these with a little solution of soda until the sublimate is dissolved; unite the solution with the ammoniacal fluid in the receivers, add hydrochloric acid, then, without filtering, chlorate of potassa, and heat gently until the sulphide of arsenic is completely dissolved. Filter from the sulphur, and determine the arsenic acid as directed § 127, 2. The quantity of tin cannot be calculated at once from the blackish-brown sulphide of tin in the bulb, since this contains more sulphur than SnS. It is therefore weighed, and the tin determined in a weighed portion of it, by converting it into binoxide, which is effected by moistening with nitric acid, and roasting (§ 126, 1, *c*).

Tin and arsenic in alloys are more conveniently converted into oxides by cautious treatment with nitric acid. If, however, it is wished to convert them into sulphides, this may readily be effected by heating 1 part of the finely divided alloy with 5 parts of carbonate of soda and 5 parts of sulphur, in a covered porcelain crucible until the mass is in a state of calm fusion. It is then dissolved in water, the solution filtered from the sulphide of iron, &c., which may possibly have formed, and then precipitated with hydrochloric acid.

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* Pharm. Centralhalle, 11, 92.

If the tin only in the alloy is to be estimated directly, while the arsenic is to be found from the difference, convert as above directed into sulphides or oxides, mix with sulphur and ignite in a porcelain crucible with perforated cover in a stream of sulphuretted hydrogen. The residual arsenic-free protosulphide of tin is to be converted into binoxide and weighed as such.

b. ARSENIC FROM ANTIMONY IN ALLOYS.

200 Heat a weighed portion of the finely divided alloy with 2 parts of carbonate of soda and 2 parts of cyanide of potassium in a bulb-tube, through which dry carbonic acid is transmitted; apply a gentle heat at first, but increase this gradually to a high degree of intensity, and continue heating until no more arsenic volatilizes. (Take care not to inhale the escaping fumes; the safest way is to insert the hind part of the bulb-tube into a flask, in which the arsenic will condense.) Allow the bulb-tube to cool; after cooling, treat the contents, first with a mixture of equal parts of spirit of wine and water, then with water, and weigh the residuary antimony. The quantity of the arsenic is found from the loss. This method gives only approximate results. If it is desired to fuse the alloy *per se* (not under a slag) in a stream of carbonic acid, the heat must be applied with great caution, otherwise antimony will volatilize to a large extent. H. ROSE recommends the latter process.

4. *Methods based upon the insolubility of Antimoniate of Soda.*

a. ANTIMONY FROM TIN AND ARSENIC (H. ROSE).

201 If the substance is metallic, oxidize the finely divided weighed sample, in a porcelain crucible, with nitric acid of 1·4 sp. gr., adding the acid gradually. Dry the mass on the water-bath, transfer to a silver crucible, rinsing the last particles adhering to the porcelain into the silver crucible with solution of soda, dry again, add eight times the bulk of the mass of solid hydrate of soda, and fuse for some time. Allow the mass to cool, and then treat with hot water until the undissolved residue presents the appearance of a fine powder; dilute with some water, and add one-third the volume of alcohol of ·83 sp. gr. Allow the mixture to stand for 24 hours, with frequent stirring; then filter, transfer the last adhering particles from the crucible to the filter by rinsing with dilute spirit of wine (1 vol. alcohol to 3 vol. water), and wash the undissolved residue on the filter, first with spirit of wine containing 1 vol. alcohol to 2 vol. water, then with a mixture of equal volumes of alcohol and water, and finally with a mixture of 3 vol. alcohol and 1 vol. water. Add to each of the alcoholic fluids used for washing a few drops of solution of carbonate of soda. Continue the washing until the color of a portion of the fluid running off remains unaltered upon being acidified with hydrochloric acid and mixed with sulphuretted hydrogen water.

Rinse the antimoniate of soda from the filter, wash the latter with a mixture of hydrochloric and tartaric acids, dissolve the antimoniate in this mixture, precipitate with sulphuretted hydrogen, and determine the antimony as directed § 125, 1. In presence of much tin it is well to fuse the antimoniate of soda again with caustic soda, &c.

To the filtrate, which contains the tin and arsenic, add hydrochloric acid, which produces a precipitate of arsenate of binoxide of tin; conduct now into the unfiltered fluid sulphuretted hydrogen for some time, allow the mixture to stand at rest until the odor of that gas has almost completely gone off, and separate the weighed sulphides of the metals which contain free sulphur, as in **199**.

If the substance contains only *antimony* and *arsenic*, the alcoholic filtrate is heated, with repeated addition of water, until it scarcely retains the odor of alcohol; hydrochloric acid is then added, and the arsenic acid determined as arsenate of magnesia and ammonia (§ 127, 2) or as sulphide of arsenic (§ 127, 4, *b*).

b. Small quantities of the sulphides of arsenic and antimony **202** mixed with sulphur are often obtained in mineral analysis. The two metals may in this case be conveniently separated as follows:—exhaust the precipitate with bisulphide of carbon, oxidize with chlorine-free red fuming nitric acid, evaporate the solution nearly to dryness; mix the residue with a copious excess of carbonate of soda, add some nitrate of soda, and treat the fused mass as given in *a* (**201**). If, on the other hand, you have a mixture of sulphides of tin and antimony to analyse, oxidize it with nitric acid of 1·5 sp. gr., and treat the residue obtained on evaporation as given in *a* (**201**).

c. DETERMINATION OF THE SULPHIDE OF ARSENIC CONTAINED IN THE COMMERCIAL SULPHIDE OF ANTIMONY (WACKENRODER).

Deflagrate 20 grm. of the finely pulverized sulphide of **203** antimony with 40 grm. nitrate of soda and 20 grm. carbonate of soda, by projecting the mixture gradually into a red-hot Hessian crucible; treat the strongly ignited mass repeatedly with water, filter the solution, acidify the filtrate with hydrochloric acid, treat with sulphurous acid, and precipitate the arsenic with sulphuretted hydrogen. Digest the moist precipitate, which contains a small admixture of antimony, with carbonate of ammonia, filter, acidify the filtrate, pass sulphuretted hydrogen, and determine the arsenic as sulphide as directed § 127, 4.

5. *Methods based upon the Precipitation of Arsenic as Arseniate of Magnesia and Ammonia.*

a. ARSENIC FROM ANTIMONY.

Oxidize the metals or sulphides with nitrohydrochloric acid, **204** with hydrochloric acid and chlorate of potassa, with bromine dissolved in hydrochloric acid, or with chlorine in alkaline solution (p. 388, *b*); add tartaric acid, a large quantity of chloride of ammonium, and then ammonia in excess. (Should the addition of the latter reagent produce a precipitate, this is a proof that an insufficient quantity of chloride of ammonium or of tartaric acid has been used, which error must be corrected before proceeding with the analysis). Then precipitate the arsenic acid as directed

§ 127, 2, and determine the antimony in the filtrate as directed in § 125, 1. As basic tartrate of magnesia might precipitate with the arsenate of magnesia and ammonia, the precipitate should always, after slight washing, be redissolved in hydrochloric acid, and reprecipitated with ammonia with addition of a little magnesia mixture.—An excellent method.

b. ARSENIOUS ACID FROM ARSENIC ACID.

Mix the sufficiently dilute solution with a large quantity of **205** chloride of ammonium, precipitate the arsenic acid as directed § 127, 2, and determine the arsenious acid in the filtrate by precipitation with sulphuretted hydrogen (§ 127, 4). LUDWIG[*] has observed that if the solution is too concentrated, arsenite of magnesia falls down with the arsenate of magnesia and ammonia, hence it is necessary to dissolve the weighed magnesia precipitate in hydrochloric acid and test the solution with sulphuretted hydrogen. The presence of arsenious acid will be betrayed by the immediate formation of a precipitate.

c. BINOXIDE OF TIN AND TEROXIDE OF ANTIMONY OR ANTIMONIC ACID FROM ARSENIC ACID.

LENSSEN[†] separated binoxide of tin from arsenic acid with **206** good results by digesting the oxides obtained by oxidation with nitric acid with ammonia and yellow sulphide of ammonium, and precipitating the arsenic from the clear solution according to § 127, 2, as arsenate of magnesia and ammonia. On acidifying the filtrate the tin separates as bisulphide. The method can only give good results when the whole of the arsenic was present as arsenic acid before the addition of sulphide of ammonium, for the arsenic in a solution of arsenious acid in yellow sulphide of ammonium is not thrown down by magnesia mixture. The method also answers for separating antimony from arsenic.

6. *Methods based on the different Behavior of the freshly Precipitated Sulphides towards Solution of Bisulphite of Potassa or Oxalic Acid.*

a. ARSENIC FROM ANTIMONY AND TIN (BUNSEN[‡]).

If freshly precipitated sulphide of arsenic is digested with sul- **207** phurous acid and sulphite of potassa, the precipitate is dissolved; on boiling, the fluid becomes turbid from separated sulphur, which turbidity for the most part disappears again on long boiling. The fluid contains, after expulsion of the sulphurous acid, arsenite and hyposulphite of potassa. [$2AsS_3 + 8(KO,2SO_2) = 2(KO,AsO_3) + 6(KO,S_2O_2) + S_3 + 7SO_2$.] The sulphides of antimony and tin do not exhibit this reaction. Both therefore may be separated from sulphide of arsenic by diluting the solution of the three sulphides in sulphide of potassium to about 500 c.c. and precipitating with a large excess (about a litre) of saturated aqueous sulphurous acid, digesting the whole for some time in a water-bath, and then boiling till one-third of the water and the whole of the sulphurous acid are expelled and the sulphur has disappeared; this will take about an hour and a half. The residuary sulphide of antimony or tin is arsenic-free, the filtrate contains the whole of the arsenic and may be immediately precipitated with sulphuretted hydrogen. **Bunsen** determines the arsenic by oxidizing the dried sulphide together with the filter with *fuming* nitric acid, diluting the solution a little, warming *gently* with a little chlorate of potassa (in order to oxidize more fully the substances formed from the paper), and finally precipitating as arsenate of magnesia and ammonia.

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[*] Archiv für Pharm. 97, 24.

[†] Annal. d. Chem. u. Pharm. 114, 116.

[‡] *Ib.* 106, 3.

With regard to the separation of sulphide of tin from the solution of arsenite of potassa it is to be observed, that the sulphide of tin must be washed with concentrated solution of chloride of sodium, as, if water were used, the fluid would run through turbid. As soon as the precipitate is thoroughly washed with the chloride of sodium, the latter is displaced by solution of acetate of ammonia, containing a slight excess of acetic acid. These last washings must not be added to the first, as the acetate of ammonia hinders the complete precipitation of the arsenious acid by sulphuretted hydrogen.

The test-analyses adduced by **Bunsen** show very satisfactory results.

b. TIN FROM ARSENIC AND ANTIMONY (F. W. CLARKE*).

Moist freshly precipitated bisulphide of tin completely dissolves on boiling for a moderate length of time with excess of oxalic acid, and therefore tin in the form of bichloride is not thrown down by sulphuretted hydrogen from a hot solution containing excess of oxalic acid. The sulphides of arsenic are barely affected by boiling with oxalic acid, and sulphuretted hydrogen immediately reprecipitates the traces dissolved. Sulphide of antimony dissolves more copiously on boiling with oxalic acid, but sulphuretted hydrogen reprecipitates the antimony from the solution. 208

To the solution of the three metals—the tin being in form of binoxide—**Clarke** recommends to add oxalic acid in quantity equal to 20 times the weight of the tin. The solution must be so strong that the oxalic acid will crystallize out on cooling. Now keeping the fluid at a boiling heat pass sulphuretted hydrogen for 20 minutes, allow to stand half an hour in a warm place and filter. According to **Clarke** the whole of the arsenic and antimony will be in the precipitate which is free or nearly free from tin. To obtain the latter from the solution, render slightly alkaline with ammonia, add sulphide of ammonium enough to redissolve the precipitate first formed, decompose the dissolved sulphosalt with excess of acetic acid, allow the precipitate of bisulphide of tin to settle in a warm place and determine it according to § 126, 1, *c*. A stronger acid than acetic which would liberate oxalic acid would not answer the purpose. **Clarke** advises, in order to increase the accuracy of the results and get the last remainder of tin into solution to redissolve the precipitated sulphides of antimony and arsenic in an alkaline sulphide, add excess of oxalic acid and boil with sulphuretted hydrogen water.

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* Chem. News, 21, 124.

From some experiments made in my laboratory by Mr. PHILLIPS, it appears that the last operation is absolutely essential, or the results will be worthless. The very unfavourable results obtained by G. C. WITTSTEIN* may perhaps be due to the presence of too much free hydrochloric acid in his solution rendering the precipitation incomplete in the heat and necessitating its being finished in the cold. In Mr. PHILLIPS's experiments the free hydrochloric acid was always neutralized as much as possible with potash.

7. *Methods based upon the Separation of the Metals themselves, or, as the case may be, on the Different Deportment of the same with Acids.*

a. TIN FROM ANTIMONY (GAY-LUSSAC, modified).

Heat a weighed portion of the finely divided alloy (or other compound) with hydrochloric acid, add chlorate of potash in small portions until the mass is dissolved, and then divide the fluid into two equal parts, *a* and *b*. In *a* precipitate both metals on a zinc rod, rinse them off quickly with hot water containing some hydrochloric acid, wash with spirit, then with ether, dry at 100° and weigh. To *b* add a rather large quantity of hydrochloric acid, introduce a strip of tin, and heat for some time. By this process, the antimony is completely thrown down in form of a black powder, and the bichloride of tin reduced to protochloride. Wash the antimony off the tin with moderately dilute hydrochloric acid, collect upon a weighed filter, wash first with dilute hydrochloric acid, then with spirit, finally with ether, dry at 100° and weigh. The difference gives the quantity of tin. **209**

From the experiments of A. W. CLASEN,† precipitated antimony is very perceptibly soluble in hot and cold hydrochloric acid of various strengths, hence loss of antimony is scarcely avoidable.

b. TIN FROM ANTIMONY (TOOKEY,‡ improvements by CLASEN (*loc. cit.*) and ATTFIELD§).

The hydrochloric solution should be oxidized if necessary with a few drops of nitric acid or a little chlorate of potash. Heat nearly to boiling and add iron as long as it dissolves. Either hoop iron or fine bright wire will answer the purpose, it should dissolve in dilute hydrochloric acid, leaving little or no residue. The antimony will be thrown down, the tin reduced to protochloride. As soon as all antimony appears to be precipitated and the iron to be dissolved, add more hydrochloric acid, allow to deposit, decant and test whether iron produces any further precipitate. In this way you will ensure the absence of any metallic iron and the complete precipitation of the antimony. Wash the antimony with hot water, which should be at first acidified, then with alcohol, finally with ether, drying at 100°. Throw down the tin with sulphuretted hydrogen (§ 127, 1, *c*). With care the results are good, compare CLASEN (*loc. cit.*). **210**

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* Vierteljahrsschr. f. prakt. Pharm. 19, 551.

† Journ. f. prakt. Chem. 92, 477; Zeitschr. f. anal. Chem. 4, 440.

‡ Journ. Chem. Soc. 15, 462.

§ Zeitschr. f. anal. Chem. 9, 107.

c. DETERMINATION OF ARSENIC IN METALLIC TIN (GAY-LUSSAC*).

211 Dissolve the laminated or granulated† metal in a mixture of 1 eq. nitric acid and 9 eq. hydrochloric acid, with the aid of a gentle heat. The solution ensues without evolution of gas; protochloride of tin and chloride of ammonium are formed, the arsenic is left in the form of powder. $NO_5 + 9HCl + 8Sn = 8SnCl + NH_4Cl + 5HO$. The nitrohydrochloric acid must, therefore, not be used in a much larger proportion than will give to 8 eq. metal 1 eq. NO_5, and 9 eq. HCl.

d. MUCH TIN FROM LITTLE ANTIMONY AND ARSENIC.

212 If an alloy of the three metals is treated in a very finely divided condition in a stream of carbonic acid with strong hydrochloric acid, the whole of the tin dissolves to protochloride. A part of the arsenic and antimony escapes as arsenetted and antimonetted hydrogen, whilst the rest remains behind in the state of metal, or, as the case may be, of a solid combination with hydrogen. Conduct the gas through several U-tubes, containing a little chlorine-free red fuming nitric acid, whereby the arsenic and antimony will be oxidized. When the solution is effected, dilute the contents of the flask with air-free water to a certain volume, mix, allow to settle and determine the tin in an aliquot part, either gravimetrically or volumetrically. Filter the rest of the fluid, wash the precipitate thoroughly, dry the filter with its contents in a porcelain crucible, add the contents of the U-tubes, evaporate to dryness, and in the residue separate the antimony and arsenic as directed **201**. It is well to treat an aliquot part of the hydrochloric solution with iron (**210**) to find, and, if necessary, estimate traces of antimony which may have passed into the hydrochloric acid solution.

e. TIN FROM GOLD.

213 Gold may be separated from excess of tin by boiling the finely divided alloy with only slightly diluted sulphuric acid, to which hydrochloric acid has been cautiously added. The tin dissolves as protochloride. Heat is applied till the sulphuric acid begins to volatilize copiously. Binoxide of tin is formed which dissolves in the concentrated sulphuric acid, while the gold remains behind. On addition of much water, the binoxide of tin falls, mixed with finely divided gold, in the form of a purple-red precipitate. On warming with concentrated sulphuric acid the binoxide of tin finally redissolves, while the gold is left pure (H. ROSE‡).

f. PLATINUM FROM GOLD.

214 The aqua regia solution is freed as far as possible from nitric acid by evaporation with hydrochloric acid, and treated with a solution of protochloride of iron, the gold being determined as directed § 123, *b*. The platinum may be precipitated from the filtrate by sulphuretted hydrogen according to § 124, *c*.

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* Annal. de Chim. et de Phys. 23, 228; Jahresber. von LIEBIG und KOPP, 1847 and 1848, 968.

† Prepared by pouring the fused metal into water.

‡ Pogg. Annal. 112, 172.

8. *Method based on the Extraction of Gold by Mercury.*

DETERMINATION OF THE GOLD IN PLATINUM ORE.

215 Treat the mineral for several hours with small quantities of pure boiling mercury, pouring off before adding a fresh portion, wash thoroughly with hot mercury, and distil off the whole of the mercury very cautiously. The gold remains behind (DEVILLE and DEBRAY.) The residue should be tested.

9. *Method based upon the Precipitation of some of the Metals as Sulphides by Hyposulphite of Soda.*

ARSENIC AND ANTIMONY FROM TIN.

216 Mix the solution with hydrochloric acid in excess, heat to boiling, and add hyposulphite of soda until the precipitate appears no longer orange or yellow, but white, and the fluid looks opalescent, owing to the separation of sulphur. Arsenic and antimony are completely precipitated, whilst the whole of the tin remains in solution (VOHL*). If arsenic alone is present in the precipitate, determine it as directed § 127, 4; if antimony alone, determine it as directed § 125, 1; if both metals are present, separate them according to **201** or **204**. The tin in the filtrate is estimated best as directed § 126, 1, *c*. LENSSEN† apparently obtained good results by this method. From my own experience I cannot speak very favourably of it. As tin is also precipitated by hyposulphite in the absence of free hydrochloric acid, the separation cannot be complete unless the hydrochloric acid present, while preventing the precipitation of tin, does not interfere with that of the antimony.

10. *Method based upon the Precipitation of Tin as Arsenate of the Binoxide.*

TIN FROM ARSENIC.

217 E. HÄFFELY‡ has proposed the following method of determining both the tin and the arsenic in commercial stannate of soda, which often contains a large admixture of arsenate of soda. Mix a weighed sample with a known quantity of arsenate of soda in excess, add nitric acid also in excess, boil, filter off the precipitate, which has the composition $2SnO_2,AsO_5 + 10$ aq., and wash; expel the water by ignition, and weigh the residue, which consists of $2SnO_2,As_5O$. In the filtrate determine the excess of arsenic acid as directed § 127, 2. The amount of the binoxide of tin is found from the weight of the precipitate, that of the arsenic acid is obtained by adding the quantity in the precipitate to the quantity in the filtrate, and deducting the quantity added.

11. *Method based on the separation of Arsenic and Antimony from their Hydrogen Compounds.*

ARSENIC FROM ANTIMONY WHEN COMBINED WITH HYDROGEN.

218 Pass the gas through neutral nitrate of silver. The antimonetted hydrogen gives antimonide of silver, while the arsenic passes into solution as arsenious acid with reduction of silver. This method has been proposed by A. W. HOFMANN* for the qualitative detection of arsenic and antimony. It may be also used as a means of quantitative separation when the metals are present in the form of hydrogen compounds. Filter off the precipitate of silver and antimonide of silver and wash it. To the solution add slight excess of hydrochloric acid, filter off the chloride of silver and precipitate with sulphuretted hydrogen. The precipitate contains the arsenic as sulphide. and always a minute quantity of sulphide of antimony; the two are to be separated according to **202** or **207**. The precipitate of silver and antimonide of silver is heated with tartaric acid and a very small quantity of nitric acid, and the antimony is estimated according to § 125, 1.

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* Annal. d. Chem. u. Pharm. 96, 240.

† *Ib.* 114, 118.

‡ Phil. Mag. 10, 220.

All methods of estimating antimony and arsenic in *solutions* on this principle (by treating with zinc and hydrochloric acid and passing the gas evolved through silver solution) are untrustworthy, since a part only of the antimony and arsenic escapes as gas, the remainder staying in the flask in the metallic form.

12. *Volumetric Methods.*

a. ARSENIOUS FROM ARSENIC ACID.

Convert the whole of the arsenic in a portion of the substance into arsenic acid and determine the total amount of this as directed § 127, 2; determine in another portion the arsenious acid as directed in § 127, 5, *a*, and calculate the arsenic acid from the difference. **219**

b. TEROXIDE OF ANTIMONY FROM ANTIMONIC ACID.

Determine in a sample of the substance the total amount of the antimony as directed § 125, 1, in another portion estimate the teroxide as directed § 125, 3, and calculate the antimonic acid from the difference. **220**

c. PROTOXIDE OF TIN IN PRESENCE OF BINOXIDE.

In one portion of the substance convert the whole of the protoxide into binoxide by digestion with chlorine water or some other means, and determine the total quantity of tin as directed § 126, 1, *b*; in another portion, which, if necessary, is to be dissolved in hydrochloric acid in a stream of carbonic acid, determine the protoxide according to § 126, 2. **221**

II. SEPARATION OF THE ACIDS FROM EACH OTHER.

It must not be forgotten that the following methods of separation proceed generally upon the assumption that the acids exist either in the free state, or in combination with alkaline bases; compare the introductory remarks, p. 406. Where several acids are to be determined in one and the same substance, we very often use a separate portion for each. The methods here given do not embrace every imaginable case, but only the most important cases, and those of most frequent occurrence.

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* Annal. d. Chem. u. Pharm. 115, 287.

FIRST GROUP.

ARSENIOUS ACID—ARSENIC ACID—CHROMIC ACID—SULPHURIC ACID—PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID—SILICIC ACID—CARBONIC ACID.

§ 166.

1. Arsenious Acid and Arsenic Acid from all other Acids.

Precipitate the arsenic from the solution by sulphuretted hydrogen (§ 127, 4, *a* or *b*), filter, and determine the other acids in the filtrate. It must be remembered, that the tersulphide of arsenic will be obtained mixed with sulphur if chromic acid, sesquioxide of iron, or any other substances which decompose sulphuretted hydrogen are present. The estimation of sulphuric acid in the filtrate cannot be accurate unless air is excluded, and oxidizers such as chromic acid are absent; sulphuric acid is, therefore, best estimated in a separate portion (**223**). From those acids which form soluble salts with magnesia, arsenic acid may be separated also by precipitation as arsenate of magnesia and ammonia (§ 127, 2). **222**

2. Sulphuric Acid from all the other Acids.*

a. From Arsenious, Arsenic, Phosphoric,† *Boracic, Oxalic, and Carbonic Acids.*

Acidify the dilute solution strongly with hydrochloric acid, mix with chloride of barium, and filter the sulphate of baryta from the solution, which contains all the other acids. Determine the sulphate of baryta as directed § 132. If acids are present with which baryta forms salts insoluble in water but soluble in acids, the sulphate of baryta is apt to carry down with it such salts, and this is all the more liable to happen, the longer the precipitate is allowed to settle. This remark applies especially to the oxalate and tartrate of baryta and the baryta salts of other organic acids (H. Rose). In such cases I would recommend, after washing, to stop up the neck of the funnel, and digest the precipitate with a solution of bicarbonate of soda, then to wash with water, with dilute hydrochloric acid, and again with water. In every case, however, the purity of the weighed sulphate of baryta must be tested as directed § 132, 1. **223**

In the fluids filtered from the sulphate of baryta the other acids are determined according to the directions of the Fourth Section, after the removal of the excess of chloride of barium. Or the other acids may be estimated in separate portions of the substance, which is indeed usually the best way, and for carbonic acid is of course the only way.

b. From Hydrofluoric Acid.

α. When sulphuric acid and hydrofluoric acid are present in the **224** free state in aqueous solution, it is best to estimate the acidity in one portion by means of standard soda (§ 215), and the sulphuric acid in another (§ 132, I., 1), finding the hydrofluoric acid by difference. The sulphate of baryta should be purified by fusion with carbonate of soda (p. 299).

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* With respect to the separation of sulphuric acid from selenic acid, comp. Wohlwill (Annal. d. Chem. u. Pharm. 114, 183).

† If metaphosphoric acid is present, it must first be converted into orthophosphoric by fusion with alkaline carbonate.

β. To estimate both acids in minerals or other dry substances, it is safest, provided the fluoride can be decomposed by sulphuric acid, to determine the fluorine in one portion according to § 138, 3, *a*, and to fuse another portion for a long time with four times its amount of carbonate of soda, which will decompose the sulphate thoroughly, the fluoride generally but partially. The fused mass is soaked in water, the solution filtered, acidified with hydrochloric acid and precipitated with chloride of barium. The sulphate of baryta thus obtained generally contains fluoride of barium and must be purified according to p. 299 by fusion with carbonate of soda, &c. **225**

γ. An actual separation of both acids may be effected, when both are in the form of alkaline salts, by adding carbonate of soda if necessary, and then precipitating the fluorine according to § 138, I., adding the chloride of calcium cautiously in very slight excess. The sulphuric acid is for the most part found in the filtrate from the carbonate of lime and fluoride of calcium, a very small part is generally also found in the acetate of lime filtered from the fluoride of calcium. Both filtrates are acidified and precipitated with chloride of barium (§ 132, I., 1. H. Rose). **226**

δ. Insoluble compounds may also be decomposed by fusion with six parts of carbonate of soda and potash, and two parts of silica. The fused mass, after cooling, is treated with water, the solution is mixed with carbonate of ammonia, and heated, more carbonate of ammonia is added to replace what evaporates, the silicic acid thrown down is filtered off and washed with water containing carbonate of ammonia, a solution of oxide of zinc in ammonia is added to precipitate the remaining silica, the fluid is evaporated till all ammonia is driven off, filtered and the process concluded as in γ. The precipitate produced by the zinc should be tested for sulphuric acid. **227**

c. From Chromic Acid.

Boil the dry compound with strong hydrochloric acid (p. 292, β) and estimate the chromic acid from the evolved chlorine. Neutralize some of the acid with ammonia, dilute and precipitate the sulphuric acid by long boiling with excess of chloride of barium. The sulphate of baryta thus obtained retains sesquioxide of chromium (H. Rose) and must always be fused with carbonate of soda &c. (p. 299). **228**

d. From Hydrofluosilicic Acid.

First throw down the hydrofluosilicic acid according to § 133, as silicofluoride of potassium, then the sulphuric acid in the filtrate with chloride of barium. **229**

e. From Silicic Acid.

Compare **242**.

3. Phosphoric Acid from the other Acids.

a. From the *acids of arsenic*, see **222**; from *sulphuric acid*, see **223**; from *silicic acid*, see **242**. **230**

b. From Chromic Acid.

Precipitate the phosphoric acid by adding nitrate of ammonia and ammonia and then nitrate of magnesia, and determine the chromic acid in the filtrate as directed § 130, I., *a*, *β* or I., *b*.

c. From Boracic Acid.

Precipitate the phosphoric acid with a solution of double chloride of magnesium and ammonium (§ 134, *b*, *a*), wash the precipitate partially, redissolve it in hydrochloric acid, reprecipitate with ammonia adding a little chloride of magnesium and ammonium, and estimate the phosphoric acid as pyrophosphate of magnesia. In the filtrate estimate the boracic acid as borate of magnesia (§ 136, I., 1, *δ*). **231**

d. From Oxalic Acid.

a. If the two acids are to be determined in one portion, the aqueous or hydrochloric solution is mixed with sodio-terchloride of gold in excess, heat applied, and the oxalic acid calculated from the reduced gold (§ 137, *c*). The gold added in excess is separated from the filtrate by sulphuretted hydrogen, and the phosphoric acid then precipitated by double chloride of magnesium and ammonium. **232**

β. If there is enough of the substance, the oxalic acid is determined in one portion according to § 137, *b*, or *d*, and the phosphoric acid in another portion. If the substance is soluble in water, and the quantity of oxalic acid inconsiderable, the phosphoric acid may be precipitated at once with chloride of magnesium, chloride of ammonium and ammonia: if not, the substance is ignited with carbonate of potash and soda, and the oxalic acid being thus destroyed, the phosphoric acid is determined in the nitric acid solution of the residue according to § 134, I., *b*, *β*. **233**

e. From Hydrofluoric Acid.

a. Phosphates and fluorides are frequently found together in minerals. In the analysis of phosphorites for instance, we have to estimate small quantities of fluorine, often too in the presence of bases such as alumina and sesquioxide of iron which increase the difficulty. According to my own experience* it is always safest in such cases to estimate in one portion the fluorine as fluoride of silicon (§ 138, II., 3, *a*), and in another portion the phosphoric acid. Regarding the first estimation it must be mentioned that carbonic acid if present must first be removed. To this end heat the finely powdered weighed substance with water, add acetic acid in slight excess, and also, if the fluoride present is soluble in water, some acetate of lime; evaporate to dryness on a water bath, treat with water, filter, wash the insoluble matter, dry, separate as far as possible from the filter, add the filter ash, weigh, test a small portion for carbonic acid by heating with hydrochloric acid, and weigh the rest for the fluorine estimation. For the estimation of the phosphoric acid, dissolve the finely powdered substance in **234** hydrochloric acid, evaporate to dryness on a water bath, moisten with a little hydrochloric acid, add nitric acid, warm, dilute, filter, evaporate filtrate and washings to dryness, dissolve in nitric acid and proceed according to § 134, I., *b*, *β*.

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* Zeitschr. f. anal. Chem. 5, 190, and 6, 403.

β. Where you have an alkaline phosphate and an alkaline fluoride together in aqueous solution, the phosphoric acid may be separated according to § 135, II., *d*, *β*, as phosphate of silver, or according to § 135, II., *k*, as phosphate of suboxide of mercury. The fluoride will be all in the filtrate. If the former method is adopted the silver is removed from the filtrate by chloride of sodium, and the fluorine estimated as calcium salt (§ 138, I.). If the latter method is adopted, as the solution is always acid, the use of glass and porcelain must be avoided. The mercury is removed from the filtrate by neutralizing with carbonate of soda and—without filtering—passing sulphuretted hydrogen. The fluorine is estimated in the filtrate as calcium salt, according to § 138, I. (H. Rose). 235

γ. Substances, which are insoluble in water, and cannot be decomposed by acids, are fused with carbonate of soda and silica (**227**), the fused mass is treated with water, and the solution with carbonate of ammonia. In this way all the fluorine and all, or nearly all, the phosphoric acid will be brought into solution. The solution is treated as in **235**, and any remainder of phosphoric acid in the undissolved residue is estimated according to **234**. 236

δ. In compounds which can be decomposed by acids the fluorine may also be occasionally estimated indirectly. Dissolve in hydrochloric acid, evaporate with sulphuric acid in slight excess, till all hydrofluoric acid has escaped (the heat must not be enough to volatilize sulphuric acid, or phosphoric acid might escape), and in the residue estimate on one hand the phosphoric acid, on the other the oxides. If now we know the proportion between the phosphoric acid and the bases in the substance, the escaped fluorine may be calculated from the excess of bases. Of course it is assumed that other acids are absent or estimated in separate portions. 237

4. HYDROFLUORIC ACID FROM OTHER ACIDS.

a. Fluorides from Borates.

Mix the solution containing alkaline borate and fluoride with some carbonate of soda, and add acetate of lime in excess. A precipitate is formed, which contains the whole of the fluorine as fluoride of calcium, and besides this, carbonate and some borate of lime; the greater portion of the latter having been redissolved by the excess of the lime salt added. Determine the fluoride of calcium in the precipitate as directed § 138, I. The small quantity of boracic acid in the precipitate is, in this process, partly volatilized, partly dissolved after evaporating the mass with acetic acid and extracting with water. It is therefore necessary to determine the boracic acid in a separate portion of the substance, according to § 136, I., 2 (A. Stromeyer).* 238

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* Annal. d. Chem. u. Pharm. 100, 91.

b. Fluorides from Silicic Acid and Silicates.

A great many native silicates contain fluorides: care must, therefore, always be taken, in the analysis of minerals, not to overlook the latter. If the silicates containing fluoride are decomposable by acids—which is only rarely the case—and the silicic acid is separated in the usual way by evaporation, the whole of the fluorine may volatilize.

a. BERZELIUS's method. Fuse the elutriated substance with 4 parts of carbonate of soda for some time at a strong red heat, digest the mass in water, boil, filter, and wash, first with boiling water, then with carbonate of ammonia. The filtrate contains all the fluorine as fluoride of sodium, and, besides this, carbonate, silicate, and aluminate of soda. Mix the filtrate with carbonate of ammonia and heat the mixture, replacing the carbonate of ammonia, which evaporates. Filter off the precipitate of hydrate of silicic acid and hydrate of alumina, and wash with carbonate of ammonia. To separate the last portions of silica from the filtrate add a solution of oxide of zinc in ammonia, evaporate till no more ammonia escapes, and filter off the precipitate of silicate and oxide of zinc. Determine the silica in this precipitate by dissolving in nitric acid, evaporating to dryness, taking up with nitric acid, and filtering off the undissolved silica. In the alkaline filtrate estimate the fluorine as calcium salt (§ 138, I.). The residue, insoluble in water, and the precipitate produced by carbonate of ammonia are finally treated with hydrochloric acid according to § 140, II., *a*, in order to the separation of the silica **239**

β. In substances readily decomposed by sulphuric acid you may also separate and weigh the silica according to **239** in one portion, and determine the fluorine in another portion according to § 138, II., 3, *a*. **240**

c. Fluorides, Silicates and Phosphates together.

Compounds of this kind are not rare in nature, and may be decomposed according to **239**. We cannot always rely on complete decomposition of the phosphate, as for instance phosphate of lime is but partially decomposed on fusion with carbonate of soda. The solution, obtained after separation of the silica by carbonate of ammonia and the zinc solution, is made up to a definite volume, and a portion is tested for phosphoric acid with molybdic solution. If none is present the fluorine is estimated in the measured remainder of the fluid as fluoride of calcium (§ 138, I.). If on the other hand phosphoric acid is still present, treat the measured remainder of the fluid according to **235**. In the original residue and the carbonate of ammonia precipitate estimate the principal amounts of the silicic and phosphoric acids and the bases. In the zinc precipitate estimate the remainder of the silicic acid, and in the filtrate from the latter estimate the portion of the phosphoric acid which was thrown down by oxide of zinc. **241**

As the phosphoric acid is so divided by this method, it is well to make a direct estimation of it in another portion of the substance, especially when only a small quantity is present. For this purpose decompose the silicate with hydrofluoric and hydrochloric acids (p. 351), add enough but not too large an excess of sulphuric acid, and evaporate till all the fluorine has escaped as fluoride of silicon and hydrofluoric acid. Do not increase the heat to the escape of sulphuric acid or phosphoric acid may be lost. Take up the residue with nitric acid, dilute, filter and estimate the phosphoric acid in the filtrate by the molybdic method (p. 307).

If the substance can be easily decomposed with sulphuric acid, the fluorine may of course also be expelled as fluoride of silicon and estimated according to § 138, II., 3, *a*.

5. SILICIC ACID FROM ALL OTHER ACIDS.

a. In compounds which are decomposed by hydrochloric acid.

Decompose the substance by digestion with hydrochloric or **242** nitric acid, evaporate the whole *on the water bath* to dryness (§ 140, II., *a*), treat with water, hydrochloric acid or nitric acid according to circumstances, filter off the silica, and estimate the other acids in the filtrate. The following points require attention.

α. In the presence of borates or fluorides this method cannot be used, employ **243**.

β. In the presence of phosphoric acid the silica always retains a small portion, which cannot be extracted by washing with acidified water (H. ROSE, W. SKEY*). After washing the silica with water, treat it repeatedly with ammonia, which will leave only a very minute quantity of the phosphoric acid. Evaporate the ammoniacal fluid, finally adding a little hydrochloric acid, dissolve in water with addition of a little nitric acid, filter off the small amount of silica which was taken up by the ammonia, and estimate the remainder of the phosphoric acid in the filtrate.

b. In compounds which are not decomposed by hydrochloric acid.

Fuse with carbonate of potash and soda (p. 348), and treat **243** the residue either at once cautiously with dilute hydrochloric or nitric acid, in order to proceed with the solution according to **242** (not applicable in presence of boracic acid or fluorine); or taking the fluid obtained by boiling the residue with water, precipitate the dissolved silica by warming with carbonate of ammonia, and throw down the last portion of silica from the filtrate by oxide of zinc dissolved in ammonia (**239**).

The silicic acid is then found partly in the residue left undissolved by water, partly in the precipitate produced by carbonate of ammonia and partly in the precipitate produced by the zinc solution. Separate it according to § 140, II., *a*. Boracic acid and fluorine will be found entirely in the last alkaline filtrate (**239**). Regarding phosphoric acid see **241**. Sulphuric acid passes for the most part into the last alkaline filtrate, yet it is well also to examine the acid filtrates from the silica.

6. CARBONIC ACID FROM ALL OTHER ACIDS.

When carbonates are heated with stronger acids, the carbonic **24** acid is expelled; the presence of carbonates, therefore, does not interfere with the estimation of most other acids. And as, on the other hand, the carbonic acid is determined by the loss of weight or by combination of the expelled gas, the presence of salts of non-volatile acids does not interfere with the determination of the carbonic acid. Accordingly, with compounds containing carbonates, sulphates, phosphates, &c., either the carbonic acid is determined in one portion, and the other acids in another, or both estimations are performed on one portion. In the latter case the process described p. 340, *e*, or p. 343, *g*, may be used with advantage, the other acids being determined in the solution remaining in the decomposing flask. In presence of fluorides, one of the weak non-volatile acids, such as tartaric acid or citric acid, must be employed to expel the carbonic acid; since, were sulphuric or hydrochloric acid used, part of the liberated hydrofluoric acid would escape with the carbonic acid. If, as will occasionally happen in an analysis, a mixed precipitate of fluoride of calcium and carbonate of lime is thrown down from a solution, the two salts may be separated by evaporating with acetic acid to dryness, and extracting the residue with water; the acetate of lime formed from the carbonate is dissolved, the fluoride of calcium is left behind.

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* Zeitschr. f. anal. Chem. 8, 70.

SECOND GROUP.

HYDROCHLORIC ACID—HYDROBROMIC ACID—HYDRIODIC ACID—HYDROCYANIC ACID—HYDROSULPHURIC ACID.

I. SEPARATION OF THE ACIDS OF THE SECOND GROUP FROM THOSE OF THE FIRST.

§ 167.

a. All the Acids of the Second Group from those of the First.

Mix the dilute solution with nitric acid, add nitrate of silver in excess, and filter off the insoluble chloride, bromide, iodide, &c., of silver. The filtrate contains the whole of the acids of the first group, the silver salts of these acids being soluble in water or nitric acid. Carbonic acid must, under all circumstances, be determined in a separate portion (§ 139, *d*, *e* or *g*). If method *d* or *g* is employed the remarks on p. 338 must be borne in mind. **245**

b. Some of the Acids of the Second Group from Acids of the First Group.

As it is often inconvenient for the further separation of the acids of the second group to have them all in the form of insoluble silver compounds, the analysis is sometimes effected by separating first the acid of the first group, then that of the second. If the quantity of substance is large enough, the most convenient way generally is to determine the several acids, *e.g.*, sulphuric acid, phosphoric acid, hydrochloric acid, sulphuretted hydrogen, &c., in separate portions. **246**

Of the infinite number of combinations that may present themselves we will here consider only the most important.

1. SULPHURIC ACID may be readily separated from chlorine, bromine, iodine, and cyanogen, by precipitation with a salt of baryta. If the acids of the second group are to be determined in the same portion, nitrate or acetate of baryta is used instead of chloride of barium. In presence of sulphuretted hydrogen, **247**

sulphuric acid cannot be determined in this way, as part of the sulphuretted hydrogen would be converted into sulphuric acid by the oxygen of the air. The error thus introduced into the process may be very considerable (FRESENIUS*). The sulphuretted hydrogen must, therefore, first be removed by chloride of copper, and the sulphuric acid determined in the filtrate; or, the sulphuretted hydrogen must be completely oxidized into sulphuric acid by chlorine or bromine, and a corresponding deduction afterwards made in calculating the quantity of the sulphuric acid. In other cases it is well to expel the sulphuretted hydrogen according to p. 389, *c*, by heating with hydrochloric acid, and to estimate the sulphuric acid in the residual fluid.

2. PHOSPHORIC ACID may be precipitated by nitrate of magnesia and ammonia, after addition of nitrate of ammonia; OXALIC ACID by nitrate of lime; chlorine, bromine, iodine, &c., are determined in the filtrate. **248**

3. CHLORIDES IN SILICATES.

a. If the silicates dissolve in dilute nitric acid, precipitate the highly dilute solution with nitrate of silver, without applying heat, remove the excess of silver from the filtrate by dilute hydrochloric acid, still without applying heat, and then separate the silicic acid in the usual way. **249**

b. If the silicate becomes gelatinous upon decomposition with nitric acid, dilute, allow to deposit, filter, wash the separated silicic acid, and treat the filtrate as in *a*.

In the processes *a* and *b* the chloride of silver may contain silica. Reduce the weighed silver salt by hydrogen and treat with nitric acid, the silica will remain behind.

c. If nitric acid fails to decompose the silicates, mix the substance with carbonate of soda and potassa, moisten the mass with water, dry in the crucible, fuse, boil with water, remove the dissolved silicic acid by carbonate of ammonia and oxide of zinc dissolved in ammonia (**239**), and then precipitate, after addition of nitric acid, with nitrate of silver.

d. If the silicates are readily decomposed by acids, chlorine may be estimated in them by heating with moderately strong sulphuric acid, and collecting the evolved hydrochloric acid in receivers, the first of which is filled with water, the second with water containing ammonia. During the operation pass a current of air through the apparatus and heat till copious fumes of sulphuric acid pass over. The apparatus, *fig. 78*, *p. 179*, will answer the purpose if provision is made for the current of air (H. ROSE). The chlorine in the contents of the receivers is estimated according to § 141, *a*.

4. CHLORIDES IN PRESENCE OF FLUORIDES.

If the substance is soluble in water, the separation may be effected as directed **245**; but it is more convenient to precipitate the fluorine with nitrate of lime, and the chlorine in the filtrate with nitrate of silver. Insoluble compounds are fused with carbonate of soda and silicic acid, and treated as in **251**. **250**

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* Journ. f. prakt. Chem. 70, 9.

5. CHLORIDES IN PRESENCE OF FLUORIDES IN SILICATES.

251 Proceed as directed **239**. Saturate the alkaline filtrate nearly with nitric acid, precipitate with nitrate of lime, separate the fluoride of calcium and the carbonate of lime as directed in **244**, and precipitate the chlorine in the filtrate by nitrate of silver.

6. SULPHIDES IN SILICATES.

252 If the substance is decomposable by acids, reduce it to the very finest powder, and treat with fuming nitric acid free from sulphuric acid (§ 148, II., 2, *a*, p. 387), or with rather dilute nitric acid in sealed tubes at 120—150° (CARIUS*). When the sulphur is completely oxidized, rinse the contents of the flask or tube into a dish, evaporate on the water bath, treat with hydrochloric or nitric acid, dilute, filter off the silica, and determine in the filtrate the sulphuric acid formed. If, on the contrary, the substance is not decomposable by acids, fuse with 4 parts of carbonate of soda and 1 part of nitrate of potassa, boil the fused mass with water, filter, remove the dissolved silicic acid from the filtrate by acidifying with hydrochloric or nitric acid and evaporating, and proceed as above directed.

7. SULPHIDES IN PRESENCE OF CARBONATES.

253 If you have to estimate sulphur in sulphides, which can easily be decomposed by acids (*e.g.*, sulphide of calcium), in presence of carbonic acid, decompose the substance by heating with hydrochloric acid, dry the evolved mixture of sulphuretted hydrogen and carbonic acid, take up the sulphuretted hydrogen by tubes filled with pumice prepared with sulphate of copper (p. 383), and the carbonic acid by soda-lime tubes (p. 341). For details see "Analysis of Black Ash," in the Special Part.

Supplement.

ANALYSIS OF COMPOUNDS, CONTAINING ALKALINE SULPHIDES, CARBONATES, SULPHATES, AND HYPOSULPHITES.

§ 168.

254 The following method was first employed by G. WERTHER† in the examination of gunpowder residues. N. FEDOROW‡ has shown that the original process included an error, which has been put right in the method described below.

Put the substance into a flask, add water, in which a sufficient quantity of carbonate of cadmium§ is suspended; cork, and shake the vessel well. The alkaline sulphide decomposes completely with the carbonate of cadmium. Filter the yellowish precipitate off, and treat it with dilute acetic acid (not with hydrochloric acid); the carbonate of cadmium dissolves, the sulphide of cadmium is left undissolved. Oxidize the latter with chlorate of potassa and nitric acid (p. 388), or with bromine (p. 388), and precipitate with chloride of barium the sulphuric acid formed from the sulphide.

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* Comp. "The determination of Sulphur in organic bodies."

† Journ. f. prakt. Chem. 55, 22.

‡ Zeitschr. f. anal Chem. 9, 127.

§ To obtain the carbonate of cadmium free from alkali, carbonate of ammonia must be used as precipitant.

Heat the fluid filtered from the yellow precipitate, and mix with solution of neutral nitrate of silver. The precipitate consists of carbonate of silver and sulphide of silver ($KO,S_2O_2 + AgO,NO_5 + HO = KO,SO_3 + AgS + HO,NO_5$). Filter it off, and wash with carbonic acid water, then remove the carbonate of silver by ammonia and precipitate the silver from the ammoniacal solution by acidifying with nitric acid and adding chloride of sodium. Each eq. chloride of silver so obtained corresponds to 1 eq. carbonate.* Dissolve the sulphide of silver in dilute boiling nitric acid, determine the silver in the solution as chloride of silver, and calculate from the result the quantity of the hyposulphite; 1 eq. AgCl corresponds to 2 eq. sulphur in hyposulphurous acid, and accordingly to 1 eq. hyposulphite (KO,S_2O_2).

From the fluid filtered from the sulphide and carbonate of silver remove first the excess of silver by means of hydrochloric acid, and then precipitate the sulphuric acid by a salt of baryta. From the sulphuric acid found you have, of course, to deduct the quantity of that acid resulting from the decomposition of the hyposulphurous acid, and accordingly for 1 part of chloride of silver formed from the sulphide, ·279 parts of sulphuric acid. The difference gives the amount of sulphuric acid originally present in the analysed compound. By way of control, you may determine, in the fluid filtered from the sulphate of baryta, the alkali as sulphate (§ 97 or § 98). Comp. "The analysis of black ash and the lie from soda residues," in the Special Part.

II. SEPARATION OF THE ACIDS OF THE SECOND GROUP FROM EACH OTHER.

§ 169.

1. HYDROCHLORIC ACID FROM HYDROBROMIC ACID.

All the methods of direct analysis hitherto proposed to effect the separation of chlorine from bromine are defective. The bromine is therefore always determined in a more indirect way.

a. Precipitate with nitrate of silver, wash the precipitate, wash 255
it from the filter into a porcelain dish, extract the filter with hot ammonia, evaporate the ammonia in a weighed porcelain crucible, add the principal quantity of the precipitate, dry, fuse, and weigh. Transfer an aliquot part of the mixed chloride and bromide of silver to a light weighed bulb-tube of hard glass,† fuse in the bulb, let the mass cool, and weigh. This operation gives both the total weight of the tube with its contents, and the weight of the portion of mixed chloride and bromide of silver in the bulb. The greatest accuracy in the several weighings is indispensable. Now transmit through the tube a slow stream of dry pure chlorine gas, heat the

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* A quantity equivalent to the sulphide found has to be deducted from this ($KS + CdO,CO_2 = CdS + KO,CO_2$). On the other hand, a quantity equivalent to the sulphide of silver must be added, for each eq. of sulphide of silver from the hyposulphite gives 1 eq. HO,NO_5, which decomposes 1 eq. carbonate of silver. This correction was overlooked by WERTHER.

† The best way of effecting the removal of the fused mass from the crucible is to fuse again, and then pour out.

contents of the bulb to fusion, and shake the fused mass occasionally about in the bulb. After the lapse of about 20 minutes, take off the tube, allow it to cool, hold it in an oblique position, that the chlorine gas may be replaced by atmospheric air, and then weigh. Heat once more for about 10 minutes in a stream of chlorine gas, and weigh again. If the two last weighings agree, the experiment is terminated; if not, the operation must be repeated once more. The loss of weight suffered, multiplied by 4·22297 (which may be taken as 4·223), gives the quantity of the bromide of silver decomposed by the chlorine. For the proof of this rule, see § 200.

This method gives very accurate results, if the proportion of bromine present is not too small; but most uncertain results in cases where mere traces of bromine have to be determined in presence of large quantities of chlorides, as, for instance, in salt-springs. To render the method available in such cases, the great point is to produce a silver compound containing all the bromine, and only a small part of the chlorine. This end may be attained in several ways. In these processes the quantity of chlorine is found by completely precipitating a separate portion with silver solution, and deducting the bromide of silver found from the weight of the precipitate.

α. Mix the solution with carbonate of soda in excess (if a precipitate is formed, do not filter), evaporate to dryness, powder the residue, extract with hot absolute alcohol; the solution contains the whole of the alkaline bromide, and only a small portion of the alkaline chloride, add a drop of soda solution, and evaporate, dissolve the residue in water, acidify with nitric acid, and precipitate with silver solution.

β. **Fehling**'s method.* Mix the solution *cold* with a quantity of solution of nitrate of silver not nearly sufficient to effect complete precipitation, shaking the mixture vigorously, and leave the precipitate for some time in the fluid, with repeated shaking. If the amount of the precipitate produced corresponds at all to the quantity of bromine present, the whole of the latter substance is obtained in the precipitate. 256

Fehling gives the following rule :—

If the fluid contains 1 bromine to 1000 chlorine use $\frac{1}{5}$ or $\frac{1}{8}$ the quantity of nitrate of silver that would be required to effect complete precipitation; if the fluid contains 10000 times as much chlorine as bromine, use $\frac{1}{10}$; if 50,000, use $\frac{1}{30}$; if 100,000, use $\frac{1}{60}$.

Wash the mixed precipitate of chloride and bromide of silver *thoroughly*, dry, ignite, weigh, and treat with chlorine as above.

γ. **Marchand**† has slightly modified **Fehling**'s method. He reduces with zinc the mixed precipitate of chloride and bromide of silver obtained by **Fehling**'s fractional precipitation, decomposes the solution of chloride and bromide of zinc with carbonate of soda, evaporates to dryness, and extracts the residue with absolute alcohol, which dissolves all the bromide of sodium with only a little of the chloride of sodium; he then evaporates the solution to dryness, takes up the residue with water, precipitates again with nitrate of silver, and subjects a part of the weighed precipitate to the treatment with chlorine. 257

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* Journ. f. prakt. Chem. 45, 269.

† *Ib.* 47, 363.

δ. If a fluid containing chlorides in presence of some bromide is heated in a retort with hydrochloric acid and binoxide of manganese, the whole of the bromine passes over before any of the chlorine. Upon this circumstance Mohr[*] bases the following method for effecting the concentration of bromine:—Distil as stated, and conduct the vapors, through a doubly bent tube, into a wide Woulf's bottle, which contains some strong ammonia. Dense fumes form in the bottle, filling it gradually. Conduct the excess of vapors from the first into a second bottle, with narrow neck, containing ammoniated water. Both bottles must be sufficiently large to allow no vapors to escape. When the whole of the bromine is evolved, which may be distinctly seen by the color of the space above the liquid in the retort and tubes, raise the cork of the flask to prevent the receding of bromide of ammonium fumes. Let the apparatus cool, and unite the contents of the two bottles; the fluid contains the whole of the bromine, with a relatively small portion of the chlorine.

b. Instead of treating the mixed chloride and bromide of silver 258
in a current of chlorine as in *a*, it may also be reduced to metallic silver, in a current of hydrogen. After accurately determining the weight of the reduced metal, calculate the amount of chloride of silver equivalent to it, subtract from this the weight of the chloride and bromide of silver subjected to the reducing process, and we have the same difference as served in *a* for the point of departure of the calculation (Wackenroder). The method has no advantage over *a*, as bromide of silver requires a very strong heat long continued for reduction in hydrogen. It will be seen that one and the same portion of mixed bromide and chloride of silver may be treated first as directed in *a*, then, by way of control, as directed in *b*. The difference found in the direct way in the first, and by calculation in the second experiment, between the weight of the mixed chloride and bromide of silver and the amount of chloride of silver equivalent to it, must be the same.

c. Fr. Mohr[†] recommends to precipitate by a known quantity 259
of silver the bromine and part of the chlorine, and to weigh the mixed precipitate of chloride and bromide of silver; which will of course again furnish the same data for calculation as in *b*. The known quantity of silver used as precipitant is either weighed off directly and dissolved in nitric acid, or added in form of a standard solution. This method is more convenient than *a*, but I do not consider it quite so accurate, more particularly for small quantities of bromine. It presupposes that a weighed quantity of silver will give an absolutely corresponding amount of chloride of silver, which practically is not the case, errors to the extent of some milligrammes being scarcely avoidable; it may accordingly happen that bromine is calculated from the supposed difference, even in cases where there is absolutely none present. Now the method *a* is not so liable to lead to such mistakes, at least not to the same extent. On the contrary, a simple experiment will show that pure chloride of silver, heated cautiously in a light bulb-tube in a current of chlorine, suffers no alteration of weight; an error occurring in this operation to the extent of ½ mgrm. is less

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[*] Annal. d. Chem. u. Pharm. 93, 80.

[†] *Ib.* 93, 76.

excusable than one to the extent of 2 mgrm. arising in the conversion of 2 or 3 grm. of silver into chloride, especially if a filter is used in the process; and this can hardly ever be dispensed with in a partial precipitation, as, in such cases, the precipitates always subside less readily and completely than in cases of complete precipitation.

d. PISANI'S method* may be looked upon as a modification of *c*. This chemist recommends to add a known quantity of nitrate of silver in slight excess, filter, and determine the silver in the filtrate by iodide of starch (p. 240). The precipitate is weighed as in *c*. This method precludes the partial precipitation. **260**

e. Determine in a portion of the solution the chlorine + bromine (by precipitating with silver), either gravimetrically or volumetrically; in another portion the bromine, either by the colorimetric method (§ 143, I., *b*, γ) or volumetrically (§ 143, I., *b*, α or β). Calculate the chlorine from the difference. The method is very suitable for an expeditious analysis of mother-liquors. **261**

f. Compare **271** and **272**.

2. HYDROCHLORIC FROM HYDRIODIC ACID.

a. Mix the solution with nitrate of protoxide of palladium, and determine the precipitated protiodide of palladium as directed § 145, I., *a*, β. Conduct sulphuretted hydrogen into the filtrate to remove excess of the palladium, destroy the excess of sulphuretted hydrogen by solution of sulphate of sesquioxide of iron, and precipitate the chlorine finally with solution of silver. It is generally found more simple and convenient to precipitate from one portion the iodine, by means of protochloride of palladium, as directed § 145, I., *a*, β, from another portion, the chlorine and iodine jointly with nitrate of silver, and to calculate the chlorine from the difference. If you have no solution of nitrate of protoxide of palladium ready, and the chlorine and iodine must be determined in one portion of the solution under examination, add a measured quantity of a solution of protochloride of palladium, determine the amount of chlorine in this in another exactly equal portion of the same solution, and deduct it. The results are accurate. In the case of fluids containing a large proportion of alkaline chlorides to a small quantity of iodide—and such cases often occur—the iodide is concentrated by adding carbonate of soda to the fluid, evaporating to dryness, extracting the residue with hot alcohol, evaporating the alcoholic solution with addition of a drop of solution of soda, and taking the residue up with water. **262**

b. Proceed exactly as for the indirect determination of bromine in presence of chlorine (**255**). The greatest care must be taken that as little as possible of the mixed chloride and iodide of silver adheres to the filter, for iodide of silver dissolves only very slightly in ammonia. Any particles of iodide of silver remaining attached to the filter may be saved by incinerating the filter and evaporating the ash with a drop of nitric acid and a drop of hydriodic acid. The loss of weight suffered by the silver precipitate on fusion in chlorine multiplied by 2·569 gives the amount of iodide of silver **263** present. The methods **259** and **260** may be also employed. These methods give in this case still better results than in the separation of bromine from chlorine, inasmuch as the difference between the equivalents of iodine and chlorine is far greater than the difference between those of bromine and chlorine. Regarding the concentration of the iodide, if necessary, see **262**.

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* Compt. rend. 44, 352; Journ. f. prakt. Chem. 72, 266.

264 *c.* Liberate the iodine by nitrous acid, take it up with bisulphide of carbon, wash the latter, and then estimate the iodine in it by hyposulphite of soda (p. 366, *β*).

In this process the chlorine is determined, either in the fluid separated from the violet bisulphide of carbon, or with greater accuracy, by precipitating the chlorine + iodine in a second portion with silver, and deducting the weight of iodide of silver corresponding to the iodine already found from the weight of the precipitate. A good and approved method.

If the quantity of iodine is small, the following method may also be used with advantage for estimating it.

The bisulphide of carbon should be thoroughly washed, covered with a layer of water, and in a stoppered bottle. Add drop by drop, with shaking, dilute chlorine water (of unknown strength), till the coloration has *just* vanished, and all the iodine is consequently converted into ICl_5. Separate the solution from the bisulphide, add iodide of potassium solution in sufficient excess, and determine the free iodine after § 146. Six parts of the iodine found correspond to 1 part originally present. If the analyst would avoid the trouble of pouring off the fluid from the bisulphide, and of washing the latter, he may transfer the mixture, after the addition of chlorine to decoloration, to a somewhat narrow measuring cylinder, note the volume occupied by the pentachloride of iodine solution, take out a portion with a pipette, and proceed as above directed.

Instead of the bisulphide, MORIDE[*] uses benzol, ROGER[†] chloroform, and instead of nitrous acid the latter chemist employs iodic acid. This last reagent was formerly proposed by v. LIEBIG for the same purpose; it is added in dilute solution to the dilute fluid mixed with sulphuric acid. It follows, from the equation $5HI + IO_5 = 5HO + I_6$, that only $\frac{5}{6}$ of the iodine here found belongs to the iodide originally present.

265 *d.* Estimate in one portion the chlorine and iodine according to § 141, I., *b*, *α*, in another portion the iodine alone according to § 145, I., *b*, *γ*, *δ* or *ε*. The chlorine is found by difference.

The method § 145, I., *b*, *δ* (PISANI'S) is very rapid, and in the presence of little chloride gives approximate results; in the presence of much chloride the results however are entirely untrustworthy, compare, p. 368. The method § 145, I., *b*, *γ* (REINIGE'S) cannot be employed if the solution contains organic matter or any substance which reduces permanganate of potash. The method § 145, I., *b*, *ε* cannot be used if the fluid contains chloric, nitrous or nitric acid.

266 *e.* For technical purposes the following method is also suitable. It was recommended by WALLACE and LAMONT[‡] for the estimation of iodine in kelp. The kelp-lie is nearly neutralized with nitric acid, evaporated to dryness, and the residue fused in a platinum vessel to oxidation of all the sulphides. Treat with water, filter, add nitrate of silver till the precipitate appears perfectly white, wash, digest with strong ammonia, and weigh the residual iodide of silver. Finally, add to the weight of the latter the amount which passes into solution in the ammonia; it is $\frac{1}{2493}$ of the aqueous ammonia (sp. gr. ·89) used.

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[*] Compt. rend. 35, 789; Journ. f. prakt. Chem. 58, 317.

[†] Journ. de Pharm. 37, 410.

[‡] Chem. Gaz. 1859, 137.

Finally compare **268, 271, 272**.

3. Chlorine, Bromine, and Iodine from each other.

267 *a.* The three metalloids are determined jointly in a portion of the fluid, by precipitating with solution of nitrate of silver (§ 141, I., *a* or *b*, *a*). To determine the iodine, another portion is precipitated with chloride of palladium in the least possible excess (§ 145, I., *a*, *β*). The fluid filtered from the precipitate is freed from palladium by sulphuretted hydrogen and the excess of the latter removed by means of sulphate of sesquioxide of iron; the chlorine and bromine are then precipitated jointly, either completely or partially with nitrate of silver and the bromine determined as directed **255**.

If the compound contains a large proportion of chlorine to a small proportion of bromine, the iodine may be precipitated also by nitrate of palladium, as there is no danger, in that case, of protobromide of palladium being coprecipitated. The filtrate is treated as above.

These methods give accurate results; but they are applicable only if the quantity of iodide present is somewhat considerable.

268 *b.* Mix the neutral dilute and cold solution containing alkaline iodide with alkaline chloride or alkaline bromide or both, with a saturated neutral solution of nitrate of thallium stirring well till, on repeated trial, you obtain a transient white precipitate—the first and permanent precipitate being yellow. It is best to have the thallium solution in a burette so that you can easily add it by drops. If the white precipitate of chloride or bromide of thallium does not at once disappear on stirring, add more water but not an unnecessary quantity or some of the iodide of thallium will remain in solution.

Allow to stand eight or twelve hours in a cold place, pour off the clear fluid through a weighed filter dried at 100°, wash the filter a little, so that no more water than necessary may pass through the precipitate, turn the precipitate on to the filter, wash with as little water as you can, dry at 100° and weigh. Precipitate the chlorine and bromine in the filtrate by silver solution. If they are both present the mixed silver precipitate is to be treated according to **255**. Results quite satisfactory (HÜBNER and SPEZIA,* and HÜBNER and

269 *c.* Remove the iodine from the solution by bisulphide of carbon, or chloroform, as in **264** In the fluid separated from the iodized bisulphide of carbon determine the chlorine and bromine as directed **255**, and in the iodized bisulphide of carbon, the iodine as directed p. 366, β. This method is particularly recommended for the separation of small quantities of iodine, and in this respect is supplementary to **267**.

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* Zeitschr. f. anal. Chem. 11, 397. † *Ib.* 11, 400.

d. Determine in a portion of the compound the chlorine, bromine, and iodine jointly by adding a known quantity of standard silver solution in slight excess, filtering and determining the small excess of silver in the filtrate by iodide of starch (p. 240). The precipitate is weighed, compare **263**. We now know the total of the chloride, bromide and iodide of silver and also the silver therein contained. **270**

Determine the iodine separately as in **269**, calculate the quantity of iodide of silver and of silver corresponding to the amount found, deduct the calculated amount of iodide of silver from the mixed iodide, chloride, and bromide of silver, that of the silver from the known quantity of the metal contained in the mixed compound; the remainders are respectively the joint amount of chloride and bromide of silver, and the quantity of the metal contained therein; these are the data for calculating the chlorine and bromine (**258**).

e. Freshly precipitated chloride of silver is converted by solution of bromide of potassium into bromide of silver, and freshly precipitated bromide and chloride of silver are converted by iodide of potassium solution into iodide of silver. Upon these facts F. Field* bases the following process for determining the three halogens when present together, in combination with metals:—Place three exactly equal portions of the substance in three stoppered bottles, add about 30 c.c. water, and silver solution in excess, shake violently, and wash the precipitates I., II., and III. completely with hot water. I. is dried and weighed, the weight represents the sum of the chloride, bromide and iodide of silver; II. and III. are digested with bromide and iodide of potassium solutions respectively for 10 hours; the solutions must be dilute, and employed in not too large excess, and without warming, otherwise they will dissolve perceptible traces of the silver salts. II. and III. are finally washed, ignited, and weighed. II. is a mixture of bromide and iodide of silver, III. is pure iodide of silver. The calculation is as follows:— **271**

a. The difference between the equivalents of bromine and chlorine (= 44·49): the eq. chloride of silver (= 143·39) : : the difference between the weights of I. and II. : the chloride of silver contained in I.

. The difference between the equivalents of iodine and bromine (= 46·90) : the eq. bromide of silver (= 187·88) : : the difference between II. and III. : the quantity of bromide of silver in II. Deduct the bromide of silver so found from the weight of II.; and the remainder is the iodide of silver.

γ. Finally subtract the sum of the chloride of silver found in *a*, and the iodide of silver found in *β*, from the precipitate I., and the remainder will represent the bromide of silver. The method is of interest from a theoretical point of view. Field's results were tolerably satisfactory.

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* Quart. Journ. Chem. Soc. 10, 234; Journ. f. prakt. Chem. 73, 404; also Chem. News, 2, 325.

The method was submitted to a searching examination by O. **Huschke**[*] and M. **Siewert**.[†] The former employed the bromide of potassium solution of the strength 1 in 48, the iodide of potassium of the strength 1 in 34, and digested for an hour. He obtained 5·248 and 5·206 grains iodine instead of 5·287, 3·313 and 3·349 grains bromine instead of 3·333, and 1·477 and 1·496 grains chlorine instead of 1·503.

Siewert worked with cold and with hot solutions, and obtained unsatisfactory results. He found that the conversion of chloride of silver into bromide is incomplete, and that on boiling bromide of silver with chloride of sodium chloride of silver is formed. He found, on the contrary, that the conversion of chloride of silver and bromide of silver into the iodide was complete.

Field's method cannot, therefore, be used, unless all the three halogens are present in relatively large quantities, and approximate results will suffice. It is absolutely inapplicable to mineral water analysis,[‡] and generally for the estimation of very small quantities of bromine and iodine in the presence of much chlorides.

272 *f.* F. **Hager**'s[§] method is based on the solubility of freshly precipitated chloride of silver in boiling solution of sesquicarbonate of ammonia, which merely takes up traces of bromide of silver, and scarcely any iodide of silver; the bromide and iodide of silver are separated by ammonia. The method only gives approximate results. In **Sonstadt**'s[‖] method the iodine is precipitated as iodate of baryta.

4. Analysis of Iodine containing Chlorine.

273 *a.* Dissolve a weighed quantity of the dried iodine in cold sulphurous acid, precipitate with nitrate of silver, digest the precipitate with nitric acid, to remove the sulphite of silver which may have coprecipitated, and weigh. The calculation of the iodine and chlorine is made by the following equations, in which A represents the quantity of iodine analysed, x the iodine contained in it, y the chlorine contained in it, and B the amount of chloride and iodide of silver obtained:—

$$x + y = A, \text{ and}$$

$$\frac{Ag + I}{I}x + \frac{Ag + Cl}{Cl}y = B$$

Now as

$$\frac{Ag + I}{I} = 1\cdot8508$$

and

$$\frac{Ag + Cl}{Cl} = 4\cdot0437$$

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[*] Zeitschr. f. anal. Chem. 7, 434.

[†] Zeitschr. f. die gesammt. Naturwiss. 1868, No. 1; Zeitschr. f. anal. Chem. 7, 469.

[‡] Yet it has been so used, 500 c.c. water being employed, see Chem. Analyse des Radeiner Sauerbrunnens, von Dr. Jos. **Mitteregger**, Vienna, 1872, W. **Braumüller**, p. 5.

[§] Pharm. Centralbl. 12, 42; Zeitschr. f. anal. Chem. 10, 341.

[‖] Chem. News, 26, 173.

we have

$$y = \frac{B - 1{\cdot}851\ A}{2{\cdot}1929}$$

b. If you have free iodine and free chlorine in solution, determine in one portion, after heating with sulphurous acid, the iodine as iodide of palladium (§ 145, I., *a*, *β*), and treat another portion as directed § 146. Deduct from the apparent amount of iodine found by the latter process, the actual quantity calculated from the iodide of palladium: the difference expresses the amount of iodine equivalent to the chlorine contained in the substance. 274

5. Analysis of Bromine containing Chlorine.

a. Proceed exactly as in **273**, weighing the bromine in a small glass bulb. Taking *A* to be equal to the analysed bromine, *B* to the bromide and chloride of silver obtained, *x* to the bromine contained in *A*, *y* to the chlorine contained in *A*, the calculation is made by the following equations:— 275

$$x + y = A$$

and

$$y = \frac{B - 2{\cdot}34997\ A}{1{\cdot}69374}$$

b. Mix the weighed anhydrous bromine with solution of iodide of potassium in excess, and determine the separated iodine as directed § 146. 276

From these data, the respective quantities of bromine and chlorine are calculated by the following equations. Let *A* represent the weighed bromine, *i* the iodine found, *y* the chlorine contained in *A*, *x* the bromine contained in *A*, then

$$x + y = A$$

$$y = \frac{i - 1{\cdot}5866\ A}{1{\cdot}9907}$$

Bunsen, the originator of methods 4 and 5, has experimentally proved their accuracy.*

6. Cyanogen from Chlorine, Bromine, or Iodine.

a. Precipitate with solution of silver, collect the precipitate upon a weighed filter, and dry in the water-bath until the weight remains constant; then determine the cyanogen by the method of organic analysis; the quantity of the chlorine, bromine, or iodine is found by difference. 277

b. Precipitate with solution of silver as in *a*, dry the precipitate at 100°, and weigh. Heat the precipitate, or an aliquot part of it, in a porcelain crucible, with cautious agitation of the contents, to complete fusion; add dilute sulphuric acid to the fused mass, then reduce by zinc, filter the solution from the metallic silver and paracyanide of silver, and determine the chlorine, iodine, or bromine in the filtrate, in the usual way by 278 silver. The cyanide of silver is the difference. NEUBAUER and KERNER* obtained very satisfactory results by this method.

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* Annal. d. Chem. u. Pharm. 86, 274, 276.

c. Precipitate with solution of silver as in *a*, weigh the precipitate and heat it, or an aliquot part, with nitric acid of 1·2 sp. gr. in a sealed tube at 100° for several hours, or at 150° for one hour. The cyanide of silver is completely decomposed, while the chloride, bromide, or iodide are unaffected. Filter the contents of the tube, wash the precipitate and weigh it, the loss indicates the amount of cyanide of silver (K. KRAUT†). 279

d. Determine the radicals jointly in a portion by precipitating with solution of silver, and the cyanogen in another portion, in the volumetric way (§ 147, I., *b* or *c*). 280

7. FERRO- OR FERRICYANOGEN FROM HYDROCHLORIC ACID.

To analyse say ferro- or ferricyanide of potassium, mixed with the chloride of an alkali metal, determine in one portion the ferro- or ferricyanogen as directed § 147, II., *g*; acidify another portion with nitric acid, precipitate with solution of silver, wash the precipitate, fuse with 4 parts of carbonate of soda and 1 part of nitrate of potassa, extract the fused mass with water, and determine the chlorine in the solution as directed in § 141. 281

8. SULPHURETTED HYDROGEN FROM HYDROCHLORIC ACID.

The old method of separating the two acids by means of a metallic salt is liable to give false results, as part of the chloride of the metal may fall down with the sulphide. We, therefore, precipitate both as silver compounds, dry the precipitate at 100°, weigh it, and determine the sulphur in a weighed portion; or—and this is usually preferred—determine in a portion of the solution the sulphuretted hydrogen as directed § 148, I., *a*, *b*, or *c*, in another portion the sulphur + chlorine in form of silver salts. If you employ a solution of nitrate of silver mixed with excess of ammonia, for the determination of the sulphuretted hydrogen, you may, after filtering off the sulphide of silver, estimate the chlorine directly as chloride of silver, by adding nitric acid, and, if necessary, more neutral silver solution. In this case you must take care that the sulphide of silver is pure: should it contain carbonate of lime, which is not unlikely if lime is present, you remove this with dilute acetic acid. The weighed sulphide of silver should be reduced by hydrogen, and then weighed again by way of control. To remove sulphuretted hydrogen from an acid solution, in order that chlorine may be determined in the latter by means of nitrate of silver, H. ROSE recommends to add solution of sulphate of sesquioxide of iron, which will effect the separation of sulphur alone; the separated sulphur is allowed to deposit, and then filtered off. 282

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* Annal. d. Chem. u. Pharm. 101, 344.

† Zeitschr. f. anal. Chem. 2, 243.

THIRD GROUP.

NITRIC ACID—CHLORIC ACID.

I. SEPARATION OF THE ACIDS OF THE THIRD GROUP FROM THOSE OF THE FIRST TWO GROUPS.

§ 170.

a. If you have a mixture of nitric acid or chloric acid with another free acid in a fluid containing no bases, determine in one portion the joint amount of the free acid, by the acidimetric method (see Special Part), in another portion the acid mixed with the chloric or nitric acid, and calculate the amount of either of the latter from the difference. 283

b. If you have to analyse a mixture of a nitrate or chlorate with some other salt, determine in one portion the nitric or chloric acid volumetrically (§ 149, II., *d*, α, β, or γ, or II., *e*, and § 150), or the nitric acid by § 149, II., *a*, β; and in another portion the other acid. I think I need hardly remark that no substances must be present which would interfere with the application of these methods. 284

c. From the chlorides of many metals whose carbonates or tribasic phosphates are insoluble, chlorates and nitrates may be separated also by digesting the solution with recently precipitated thoroughly washed carbonate or tribasic phosphate of silver in excess, and boiling the mixture. In this process, the chlorides transpose with the carbonate or phosphate—chloride of silver and carbonate or phosphate of the metal with which the chlorine was originally combined being formed, which both separate, together with the excess of the carbonate or phosphate of silver, whilst the chlorates and nitrates remain in solution (H. ROSE, CHENEVIX, LASSAIGNE[*]). 285

d. The estimation of an alkaline chlorate, in presence of a chloride, may be effected also by precipitating one portion at once, and another portion after gentle ignition, with solution of silver, and calculating the chloric acid from the difference between the two precipitates. Or determine the chlorine with silver solution in one portion at once, and in another portion after reducing the chloric acid with nitrous acid or protoxide of iron (§ 150, II., *c* and *d*). 286

e. Where you have nitrate of soda or potash in presence of nitrite or carbonate, as for instance in the commercial alkaline nitrites, estimate in one portion the carbonate by standard acid according to § 219,[†] in another portion the nitrous acid by permanganate or chromate of potash (p. 298). The nitrate is found by difference. 287

For the estimation of nitric and nitrous acids, the base being either potash or soda, an indirect method may also be employed. Mix the weighed substance intimately with chloride of ammonium, heat moderately in a porcelain crucible till the excess of chloride of ammonium and the products of decomposition are expelled, dissolve the residue in water, and titrate say the chloride of sodium with silver solution (§ 141, I., *b*, *a*). After deducting the carbonate of soda, if any is present, from the weight of the substance taken, and the chloride of sodium equivalent to it from the chloride of sodium found, you will have the necessary basis for the calculation as follows: From the remaining chloride of sodium thus obtained calculate the equivalent quantity of nitrate of soda, and deduct therefrom the total weight of the nitrate and nitrite of soda, the remainder will correspond to the nitrite of soda, which may be obtained by the following proportion:—16 (the difference between the equivalents of nitrate and nitrite of soda) : 69·08 (the equivalent of nitrite of soda) :: the remainder in question : x, x being the quantity of nitrite of soda in the substance taken. Finally, deduct the carbonate and nitrite of soda from the substance taken, and the remainder will be the nitrate of soda. Of course it is understood that no extraneous substances are present. Compare TICHBORNE* and my own report upon the method.† A similar indirect method may be based on the expulsion of nitrous, nitric (and carbonic) acids by vitrified borax (§ 139, II., *c*. and § 149, II., *a*, *β*), and also on the different oxidizing action of nitrous and nitric acid on sulphate of iron mixed with hydrochloric acid (p. 394), compare C. D. BRAUN.‡

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[*] Journ. de Pharm. 16, 289; Pharm. Centralbl. 1850, 121.

[†] The alkaline nitrites have no alkaline reaction.

II. SEPARATION OF THE ACIDS OF THE THIRD GROUP FROM EACH OTHER.

We have as yet no method to effect the direct separation of nitric acid from chloric acid; the only practicable way, therefore, is to determine the two acids jointly in a portion of the compound, by the method described for nitric acid § 149, II., *d*, *β*, and for chloric acid § 150, II., *b*. In another portion estimate the chloric acid, by adding carbonate of soda in excess, evaporating to dryness, fusing the residue until the chlorate is completely converted into chloride, and then determining the chlorine in the latter, taking care that the chloride of silver contains no difficultly soluble nitrite. 1 eq. chloride of silver produced from this corresponds to 1 eq. chloric acid, provided there was no chloride originally present. 288

* Chem. News, 1865, 304.

† Zeitschr. f. anal. Chem. 4, 446.

‡ *Ib.* 6, 47.

INDEX.

AIR-BATHS, 45, 47, 48, 49
Air-pump, hydraulic, 76
Alumina, est., 192
— solution of native compounds, 191
— conversion of al. salts into, 193
— pp. in pure sols., 192
— sep. from alkalies, 4 3
— sep. from alk. earths, *Index*, 424
— sep. from chromium, 428
— sep. from metals of Gr. IV., *Index*, 433
— fe. mn. ca. mg. k. na., sep. from each other, 449
— properties, 126
Ammonia, est., 177
— indirect est., 180
— expelled by distillation, 178
— expelled in the cold, 179
— sep. from other alkalies, *Index*, 407
Ammonia arsenio-molybdate, properties, 158
Ammonia carbonate, tests of purity, 101
— uses as reagent, 101
Ammonia nitrate, preparation, 101
— tests of purity, 101
— uses as reagent, 101
Ammonia phosphate, preparation, 95
— tests of purity, 96
Ammonia phospho-molybdate, pp., 307
— properties, 163
Ammonia succinate, preparation, 96
— use as reagent, 96
Ammonium chloride, properties, 116
— conversion of am. salts into, 177
— uses as reagent, 101
Ammonium and h. fluoride, preparation, 100
— tests of purity, 101
— uses as reagent, 101
Ammonium and pt. chloride, properties, 117
— pp. in pure sols., 178
— conversion into pt., 178
Antimonic acid, sep. from sb. teroxide, 494
Antimonious acid, properties, 153
Antimony, est., 272
— properties, 154
— tit. by iodine, 275
— tit. by permanganate, 276
— tit. by bichromate, 275
— tit. of sulphide, 277
Antimony, sep. from metals of Gr. I.—V., *Index*, 473
— sep. from metals of Gr. VI., *Index*, 485
Antimony antimonate, conversion of sb. compounds into, 273
Antimony sulphide, pp. in pure sols., 272
— properties, 153
Antimony teroxide, sep. from antimonic acid, 494
Anvil, 40
Arsenate iron, properties, 158
Arsenate lead, conversion of as. compounds into, 283
— properties, 156
Arsenate magnesia, properties, 157
Arsenate magnesia and ammonia, pp. in pure sols., 283
— properties, 156
Arsenate uranium, properties, 157
— pp. in pure sols., 284
Arsenic, est., 282
— tit by bichromate, 286
— tit. by hyposulphite, 287
— tit. by iodine, 286
— tit. by uranium, 287
— sep. from metals of Gr. I.—V., *Index*, 473
— sep. from metals of Gr. VI., *Index*, 485
Arsenic acid, sep. from arsenious acid, *Index*, 485
— sep. from all other acids, 495
Arsenic sulphide, properties, 156
— pp. in pure as. sols., 284
— pp. in sulphur sols., 382
Arsenio-molybdate ammonia, properties, 158
— pp. in pure sols., 284
Arsenious acid, sep. from arsenic acid, *Index*, 485
— sep. from all other acids, 495
— tests of purity, 105
— uses as reagent, 105
Azotometer, 400

BALANCE, 10
—tested, 14
— theory, 10
Barium chloride, purification, 97
Barium silicofluoride, properties, 119
Baryta, est., 182

Baryta, sep. from alkalies, *Index*, 413
— sep. from other alk. earths, *Index*, 418
Baryta acetate, preparation, 97
— tests of purity, 97
— uses as reagent, 98
Baryta carbonate, pp. in pure sols., 183
— conversion of ba. salts into, 183
— properties, 119
Baryta chromate, properties, 159
— pp. in pure chromate sols., 291
Baryta sulphate, properties, 118
— pp. in pure ba. sols., 182
— pp. in pure sulphate sols., 299
— conversion of ba. salts into, 183
Bismuth, est., 262
— conversion of bi. compounds into, 264
— sep. from metals of Gr. I.—IV., *Index*, 456
— sep. from metals of Gr. V., *Index*, 463
— properties, 149
Bismuth arsenate, pp. in pure sols., 265
Bismuth carbonate, properties, 149
— pp. in pure sols., 263
Bismuth chloride, basic, properties, 149
Bismuth chromate, properties, 150
— pp. in pure sols., 264
Bismuth nitrate, basic, properties, 149
Bismuth oxide, properties, 149
— conversion of bi. compounds into, 263
Bismuth sulphide, properties, 150
— pp. in pure sols., 263
Blende, solution, 197
Boracic acid, est., 320
— sep. from bases, 322
Borates, analysis, 322
Borax, fused, preparation, 99
— uses as reagent, 100
Bromides, analysis, 365
Bromine, est., 362
— tit. by silver, 363
— tit. by silver and iodide starch, 363
— tit. by alkalimetry, 363
— tit. by chlorine, 363
— sep. from acids of Gr. I., 501
— sep. from metals, 365
— sep. in chlorides, 504
— free, est., 365
— containing chlorine, analysis, 512
Burette, fitted, 32
— GAY-LUSSAC'S, 36
— GEISSLER'S, 37
— holder, 34
— reading off, 34
— tested, 35

CADMIUM, est., 266
— tit. by oxalic acid, 267
— sep. from metals of Gr. I.—IV., *Index*, 456
— sep. from metals of Gr. V., *Index*, 463
Cadmium carbonate, properties, 151
— pp. in pure sols., 266
Cadmium oxide, properties, 150
— conversion of cd. compounds into, 266
Cadmium sulphate, conversion of cd. compounds into, 267
Cadmium sulphide, properties, 151
— pp. in pure sols., 266
Calcium, see *Lime*
Calcium chloride, preparation, 109
— uses as reagent, 110
Calcium fluoride, properties, 164
— precipitation, 326
Carbon bisulphide, purification, 91
— uses as reagent, 91
Carbonates, analysis, 336
Carbonic acid, est., 330
— sep. from other acids, 500
— sep. from bases, 336
Carbonic acid apparatus
— FRESENIUS and WILL'S, 337
— MOHR'S, 339
— GEISSLER'S, 339
— SCHEIBLER'S, 343
— RUMPF'S, 346
Chlorates, analysis, 403
Chloric acid, est., 403
— reduction to chlorine, 403, 404
— tit. by hyposulphite, 403
— tit. by tin protochloride, 403
— tit. by lead, 404
— sep. from nitric acid, 515
— sep. from other acids, 514
Chlorides, analysis, 359
Chlorine, est., 354
— est. in presence of free chlorine, 362
— tit. by silver, 355
— tit. by alkalimetry, 358
— tit. by silver and iodide starch, 356
— tit by hg. nitrate, 357
— free, est., 360
— free, tit. by k. iodide, 361
— sep. from metals, 359
— sep. from acids of Gr. I., 501
— sep. in silicates, 502
— sep. in fluorides, 502
— sep. in silicates containing fluorides, 503
— purification, 102
— uses as reagent, 102
— bromine and iodide, sep., 509
— gas, preparation, *foot note*, 384
Chromates, analysis, 293
Chromic acid, est., 290
— est. by oxalic acid, 291
— reduction to sesquioxide, 290
— tit. by iron, 291
— tit. by hyposulphite, 292
— tit. by other methods, 293
— sep. from bases, 293
Chromium, est., 194
— sol. of native compounds, 194
— sep. from alkalies, 423
— sep. from alk. earths, *Index*, 424
— sep. from alumina, 428
— sep. from metals of Gr. IV., *Index*, 433
Chromium oxide, conversion of cr. compounds into, 195

Chromium oxide, conversion into chromic acid, 195
— properties, 127
— pp. in pure sols., 194
Clip for burettes, 32
— for watch-glasses, 44
Cobalt, est., 210
— tit. with permanganate and hg. oxide, 212
— sep. from alkalies, 429
— sep. from alk. earths, *Index*, 430
— sep. from metals of Gr. III. and IV., *Index*, 434
— conversion of co. salts into, 210
— properties, 135
— preparation of pure, *foot note*, 212
Cobalt protoxide, properties, 134
— pp. in pure sols., 211
Cobalt sesquioxide and potash nitrite, pp. in pure sols., 211
Cobalt sulphate, properties, 136
— conversion of co. salts into, 212
Cobalt sulphide, properties, 135
— pp. in pure sols., 211
Copper, est., 254
— conversion of cu. oxide into, 257
— properties, 146
— pp. as such in pure sols., 256
— tit. by hyposulphite, 258
— tit. by k. cyanide, 259
— tit. by na. sulphide, 260
— tit. by tin protochloride, 261
— tit. by various methods, 261
— sep. from metals of Gr. I.—IV., *Index*, 456
— sep. from metals of Gr. V., *Index*, 463
— preparation of pure, 95
— preparation for organic analysis, 108
— tests of purity, 95
— uses as reagent, 95
— use in organic analysis, 108
Copper oxide, properties, 147
— conversion of cu. salts into, 256
— pp. in pure sols., 255
— preparation, 106
— tests of purity, 106
— use as reagent, 107
— spent, recovery, 107
Copper suboxide, properties, 148
Copper subsulphide, properties, 148
— conversion of cu. compounds into, 258
Copper subsulphocyanide, properties, 148
— pp. in pure sols., 258
Copper sulphide, properties, 147
— pp. in pure cu. sols., 257
— pp. in sulphur sols., 382
Crucible tongs, 84
Cyanides, analysis, 375
Cyanogen, est., 373
— tit. by silver, 374
— tit. by iodine, 375
— sep. from acids of Gr. I., 501
— sep. from chlorine, bromine and iodine, 512
— sep. from metals, 375

DECANTATION, 68, 79
Desiccators, 41
Distilled water, 90
Drying, 40
Drying disk, 51

ELUTRIATION, 39
End reaction, 89
Ether, use as reagent, 90
Evaporation, 60
— action of fluids on vessels during, 65

FERRICYANOGEN, tit. with permanganate, 379
— tit. with hyposulphite, 379
— sep. from chlorine, 513
Ferrocyanogen, tit. with permanganate, 378
— tit. with bichromate, *foot note*, 378
— tit. with cu. sulphate, 380
— tit. in presence of sulphocyanogen, 380
— sep. from chlorine, 513
Filter, asbestos, 79
— glass, 79
— sand, 79
— patterns, 70
— stands, 70
— tubes, 79
Filtering, by suction, 74
— rules in, 71
Final reaction, 89
Float, burette, 35
Fluorides, analysis, 326
— est. in silicates, 499
Fluorine, est., 326
— sep. from metals, 326
— sep. from other acids, 498

GASES, rules in measuring, 22
— vessels for measuring, 20
Gold, est., 268
— conversion of gold compounds into, 269
— pp. as such in pure sols., 269
— properties, 151
— sep. from metals of Gr. I.—V., *Index*, 473
— sep. from metals of Gr. VI., *Index*, 485
Gold sulphide, properties, 151
— pp. in pure sols., 270
Gunpowder residues, analysis, 503

HYDRIODIC acid, see *Iodine*
Hydrobromic acid, see *Bromine*
Hydrochloric acid, see *Chlorine*
— preparation, 92
— tests of purity, 92
— uses as reagent, 92
Hydrocyanic acid, see *Cyanogen*

Hydrofluoric acid, see *Fluorine*
— preparation, 92
— tests of purity, 92
— uses as reagent, 92
Hydrofluosilicic acid, est., 304
Hydrogen, preparation, 101
— tests of purity, 101
— uses as reagent, 101
Hydrosulphuric acid, see *Sulphur*
Hyponitric acid, est., 298
Hyposulphites, analysis, 297
Hyposulphurous acid, est., 297
— tit. by iodine, 297

IGNITION in hydrogen, 200
Iodates, analysis, 297
Iodic acid, est., 297
Iodides, analysis, 368
Iodine, est., 365
— tit. by silver, 366
— tit. by silver and iodide starch, 366, 367
— tit. by alkalimetry, 366
— tit. by nitrous acid and bisulphide carbon, 366
— tit. by permanganate, 367
— tit. by various methods, 368
— sep. from metals, 368
— sep. from acids of Gr. I., 501
— free, est., 369
— free, tit. by hyposulphite, 370
— containing chlorine, analysis, 511
— sep. in chlorides, 507
— preparation, 104
— tests of purity, 104
— use as reagent, 104
Iron, est., 213
— tit. by bichromate, 220
— tit. by permanganate, 215
— tit by hyposulphite, 227, 228
— tit. by tin protochloride, 225
— sep. from alkalies, 429
— sep. from alk. earths, *Index*, 430
— sep. from metals of Gr. III. & IV., *Index*, 434
— al. mn. ca. mg. k. na., sep. from each other, 449
Iron acetate, basic, properties, 138
Iron and ammonia sulphate, preparation, 104
— tests of purity, 104
— use as reagent, 104
Iron arsenate, properties, 158
Iron formate, basic, properties, 139
Iron phosphate, properties, 160
— precipitation, 311
Iron protoxide, conversion into sesquioxide, 214
— sep. from sesquioxide, *Index*, 434
— solution of native compounds, 213
Iron sesquioxide, properties, 136
— conversion of iron salts into, 223
— pp in pure sols., 222
— reduction to protoxide, 224
Iron sesquioxide, sep. from protoxide, *Index*, 434
— solution of native compounds, 221
Iron succinate, properties, 138
Iron sulphide, properties, 137
— conversion of iron compounds into, 223
— pp. in pure sols., 222

LEAD, est., 241
— conversion of lead salts into, 246
— tit. by oxalic acid, 247
— tit. by bichromate, 247
— tit. by standard acid, 247
— sep. from metals of Gr. I.—IV., *Index*, 456
— sep. from metals of Gr. V., *Index*, 463
Lead arsenate, properties, 156
Lead carbonate, properties, 141
— pp in pure sols., 243
Lead chloride, properties, 143
— pp. in pure sols., 245
Lead chromate, properties, 159
— pp. in pure lead sols., 245
— pp. in pure chromate sols., 291
— preparation, 107
— tests of purity, 107
— use as reagent, 107
— spent, recovery, 107
Lead oxide, properties, 142
— conversion of lead salts into, 243
— preparation, 95
— uses as reagent, 95
Lead phosphate, properties, 160
— conversion of phosphoric acid into, 306
Lead sulphate, properties, 142
— conversion of lead salts into, 244
— pp. in pure sols., 244
Lead sulphide, properties, 143
— pp. in pure sols., 243
Levigation, 39
Lime, est , 185
— titration, 189
— sep. from alkalies, *Index*, 413
— sep. from other alk. earths, *Index*, 418
— properties, 123
— purification from alkalies, 93
Lime carbonate, properties, 121
— pp. in pure sols, 186
Lime oxalate, properties, 122
— pp. in pure lime sols., 187
— pp. in oxalic acid sols., 324
— titration, 189
Lime sulphate, properties, 121
— conversion of lime salts into, 186
— pp. in pure sols, 186
Lithia, est., 181
— sep. from other alkalies, *Index*, 407
Lithia, carbonate, properties, 181
Lithia phosphate, properties, 181
— pp. in presence of alkalies, 181
Lithia sulphate, properties, 181

Lithium chloride, properties, 181
Litmus tincture, preparation, 102
— tested, 103

MAGNESIA, est., 189
— properties, 125
— conversion of mg. salts into, 191
— sep. from alkalies, *Index*, 413
— sep. from other alk. earths, *Index*, 418
Magnesia and ammonia arsenate, properties, 156
Magnesia and ammonia phosphate, properties, 124
— pp. in pure mg. sols., 190
— pp. in pure phosphate sols., 306
Magnesia arsenate, properties, 157
Magnesia mixture, preparation, 98
— improved, preparation, *foot note*, 307
Magnesia phosphate, properties, 160
— conversion of phosphates into, 312
Magnesia pyrophosphate, properties, 124
Magnesia sulphate, properties, 123
— conversion of mg. salts into, 198
— uses as reagent. 98
Manganese, est., 201
— tit. by k. ferricyanide, 205
— tit. by permanganate, 206
— tit. by boiling with hydrochloric acid, 207
— sep. from alkalies, 429
— sep from alk. earths, *Index*, 430
— sep from metals of Gr. III. and IV., *Index*, 433
Manganese and ammonia phosphate, properties, 132
— pp. in pure sols., 205
Manganese binoxide, properties, 131
— pp. in pure sols., 203
Manganese carbonate, properties, 130
— pp. in pure sols., 202
Manganese protoxide, properties, 130
— pp. in pure sols, 202
Manganese protosesquioxide, properties, 131
— conversion of mn. compounds into, 203
Manganese sulphate, properties, 132
— conversion of mn. compounds into, 204
Manganese sulphide, properties, 131
— conversion of mn. compounds into, 204
— pp. in pure sols., 204
Measuring flasks, tested, 27
Mercurial trough, 23
Mercury, properties, 144
— est., 248
— pp. as such in pure sols., 251
— conversion of hg. salts into, 250
— tit. by na. chloride and na. phosphate, 252
— tit. by na. chloride, 248, 252
— tit. by iodine, 249
— sep. from metals of Gr. I.—IV., *Index*, 456
— sep. from metals of Gr. V., *Index*, 463
Mercury chromate, properties, 159
— pp. in pure chromate sols., 291
Mercury oxide, properties, 146
— conversion of hg salts into, 252
— sep. from suboxide, 464
— preparation, 95
— test of purity, 95
— uses as reagent, 95
Mercury phosphate, properties, 162
— precipitation, 308
Mercury subchloride, properties, 144
— pp. in pure sols., 248, 251
Mercury suboxide, sep. from oxide, 464
Mercury sulphide, properties, 145
— pp. in pure sols., 251
Metaphosphoric acid, conversion into phosphoric, 306
Molybdate lead, pp in pure sols., 289
Molybdate mercury, pp. in pure sols., 289
Molybdenum, est., 289
— tit. by permanganate, 290
Molybdenum binoxide, conversion of mo. compounds into, 289
Molybdenum sulphide, pp. in pure sols., 289
Molybdic acid residues, recovery, 96
Mortar, steel, 38

NICKEL, est., 207
— titration, 209
— conversion of ni. compounds into, 209
— sep. from alkalies, 429
— sep. from alk. earths, *Index*, 430
— sep. from metals of Gr. III. and IV., *Index*, 434
— properties, 133
Nickel protoxide, properties, 133
— conversion of ni. salts into, 209
— pp. in pure sols., 208
Nickel sulphate, properties, 133
— conversion of ni. salts into, 209
Nickel sulphide, properties, 134
— pp. in pure sols , 208
Nitrates, analysis, 390
Nitric acid, est., 390
— est. by azotometer, 399
— conversion into nitrogen, 402
— distillation, 391
— expulsion in dry way, 390
— tit. by permanganate or bichromate, 392
— tit. by tin protochloride, 394
— tit. by SCHLOSING's method, 395
— tit. by conversion into ammonia, 397
— sep. from bases, 390
— sep. from chloric acid, 515
— sep. from other acids, 514
— preparation, 91
— tests of purity, 91
— uses as reagent, 91
Nitrites, analysis, 298
Nitrogen, properties, 117
Nitrous acid, estimation, 298
— tit. by permanganate, 298
Normal solutions, 88

OIL BATHS, 49, 50
Oxalates, analysis, 325
Oxalic acid, est., 324
— conversion into carbonic acid, 324
— tit. by permanganate, 324
— sep. from bases, 325
— preparation, 102
— tests of purity, 102
— uses as reagent, 102
Oxygen, preparation, 107
— tests of purity, 108

PALLADIUM, est., 267
— pp. as such in pure sols., 267
— properties, 268
Palladium cyanide, pp. in pure sols., 267
Palladium iodide, properties, 167
— precipitation, 365
Palladium and potassium chloride, properties, 268
— pp. in pure sols., 268
Palladium sulphide, pp. in pure sols., 267
Phosphates, analysis, 314
Phosphoric acid, est., 305
— tit. by uranium, 312
— sep. from bases, 314
— sep. from other acids, 497
Pyrophosphoric acid, conversion into phosphoric, 306
Platinum, properties, 152
— est., 270
— conversion of pt. compounds into, 271
— pp. as such in pure sols., 271
— sep. from metals of Gr. I.—V., *Index*, 473
— sep. from metals of Gr. VI., *Index*, 485
— crucibles, 83
Platinum and am. chloride, properties, 117
— pp. in pure pt. sols., 270
Platinum and k. chloride, properties, 114
— pp. in pure pt. sols., 271
Platinum bichloride, strength of sol., 99
Platinum sulphide, properties, 152
— pp. in pure sols., 271
Potassa, est., 171
— sep. from other alkalies, *Index*, 407
— preparation of pure sol., 93
— preparation for organic analysis, 109
Potassa bichromate, purification, 110
— uses as reagent, 110
Potassa bisulphate, properties, 113
— preparation, 100
— uses as reagent, 100
Potassa nitrate, properties, 113
— conversion of k. salts into, 173
Potassa permanganate, preparation, 103
Potassa sulphate, properties, 112
— conversion of k. salts into, 172
Potassium borofluoride, properties, 163
— pp. in boracic acid sols., 321
Potassium chloride, properties, 113
— conversion of k. salts into, 173
Potassium cyanide, preparation, 97
Potassium and h. fluoride, preparation, 100
— tests of purity, 100
— uses as reagent, 100
Potassium iodide, preparation, 104
— tests of purity, 104
— uses as reagent, 105
Potassium and pt. chloride, properties, 114
— pp. in pure sols., 173
Potassium silicofluoride, properties, 114
— pp. in pure k. sols., 175
— pp. in hydrofluosilicic acid sols., 304
— titration, 175
Pipettes, tested, 30
— used, 29
Powdering, 38
Precipitates, dried, 80
— ignited, 82
— washed, 73
Precipitation, 67

SELENATES, analysis, 296
Selenious acid, est., 295
— sep. from bases, 295
Selenium, pp. as such, 295, 296
Selenites, analysis, 295
Selenium sulphide, pp., 295
Sifting, 39
Silicates analysis, 347
— by acids, 347
— by acids in sealed tubes, 354
— by alk. carbonates, 348
— by hydrofluoric acid solution, 350
— by hydrofluoric acid gas, 351
— by am. fluoride, 352
— by k. and h. fluoride, 352
— by baryta or ba. carbonate, 352
— by lime and lime salts, 353
Silicic acid, est., 346
— properties, 165
— sep. from bases, 347
— sep. from other acids, 500
— tested, 348
Silicofluorides, analysis, 305
Silver, est., 231
— properties, 139
— solution of insoluble salts, 231
— conversion of ag. compounds into, 234
— pp. as such in pure sols., 235
— tit. by na. chloride, 235
— tit. by iodide starch, 240
— tit. by na. chloride in presence of k. chromate, 241
— sep. from metals of Gr. I.—IV., *Index*, 456
— sep. from metals of Gr. V., *Index*, 463
— preparation, 106
— preparation of pure, *foot note*, 285
— use as reagent, 106
Silver bromide, properties, 166
— pp. in bromide sols., 362
Silver chloride, properties, 139
— conversion of ag. salts into, 232

Silver chloride, pp. in ag. sols., 232
— pp. in chloride sols., 354
Silver cyanide, properties, 141
— pp. in ag. sols., 234
— pp. in cyanide sols., 373
Silver iodide, properties, 167
— precipitation, 365
Silver phosphate, properties, 162
Silver sulphide, properties, 140
— pp. in ag. sols., 233
— pp. in sulphur sols., 382
Soda, est., 175
— sep. from other alkalies, *Index*, 407
Soda bisulphate, properties, 115
— preparation, 100
— uses as reagent, 100
Soda carbonate, properties, 116
— conversion of soda salts into, 176
Soda hyposulphite, tests of purity, 96
— uses as reagent, 96
— preparation of standard sol., 371
Soda nitrate, properties, 115
— conversion of soda salts into, 176
Soda sulphate, properties, 115
— conversion of soda salts into, 176
Soda lime, preparation, 108
— tests of purity, 108
— uses as reagent, 108
Sodium chloride, properties, 115
— conversion of soda salts into, 176
— preparation, 106
— tests of purity, 105
— uses as reagent, 106
Sodium and pt. chloride, properties, 116
Sodium silicofluoride, properties, 116
Solution, 58
Standard solutions, 88
Strontia, est., 184
— sep. from alkalies, *Index*, 413
— sep. from alk. earths, *Index*, 418
Strontia carbonate, properties, 120
— conversion of sr. salts into, 185
— pp. in pure sols., 185
Strontia sulphate, properties, 120
— conversion of sr. salts into, 185
— pp. in pure sols., 184
Strontium chloride, preparation, 98
— uses as reagent, 98
Sulphates, analysis, 303
Sulphides analysis, 383
— by nitrates, 383
— by chlorates, 384
— by chlorine, dry, 384
— by chlorine, wet, 388
— by hg. oxide, 386
— by nitric acid, 387
— by k. chlorate and hydrochloric acid, 387
— by k. chlorate and nitric acid, 388
— by aqua regia, 388
— by bromine, 388
Sulphites, analysis, 296
Sulphur, est., 380
— sep. as such from sols., 389
Sulphur, tit. with soda arsenite, 382
— tit. with copper, 389
— tit. with silver, 389
— tit. with iodine, 381
— sep. from metals, 383
— sep. from acids of Gr. I., 501
— sep. in silicates, 503
— sep. in carbonates, 503
— sep. from chlorine, 513
Sulphuretted hydrogen, est. of gas, 380, 383
Sulphuric acid, est., 298
— est. in presence of sulphates, 304
— tit. by ba. chloride, 299
— tit. by lead, 303
— sep. from other acids, 495, 501
— sep. from bases, 303
Sulphurous acid, est., 296
— est. as sulphuric acid, 297
— tit. by iodine, 296
— preparation, 105
— uses as reagent, 105
Swedish filtering paper, 69

TENSION of aqueous vapor, 26
Tin, est., 277
— solution of insoluble compounds, 277
— tit. by iodine, 280
— tit by permanganate, 280
— sep. from metals of Gr. I.—V., *Index*, 473
— sep. from metals of Gr. VI., *Index*, 485
Tin binoxide, properties, 154
— conversion of tin compounds into, 278
— pp. in pure sols., 279
— sep. from protoxide, 494
Tin phosphate, properties, 162
— precipitation, 309
Tin protochloride, preparation of standard sol., 226
Tin protoxide, sep. from binoxide, 494
Tin sulphides, properties, 155
— pp. in pure sols., 279
Titanic acid, est., 196
— properties, 196
— titration, 197
Titration, 88

URANIUM, est., 229
— tit. by permanganate, 230
— sep. from alkalies, 429
— sep. from metals, of Gr. I.—IV., 453
Uranium acetate, preparation, 98
— tests of purity, 99
— uses as reagent, 99
Uranium ammonio-sesquioxide, pp. in pure sols., 229
Uranium arsenate, properties, 157
Uranium phosphate, precipitation, 311
— properties, 161
Uranium protosesquioxide, conversion of u. salts into, 229

Uranium protosesquioxide, reduction to protoxide, 230 .
Uranium residues, recovery, 99

WASHING, bottles, 72
— rules in, 72
Water, baths, 44, 46
— est., 54
Weighing off, 53
— theory, 16
— rules in, 18
— by substitution, 17
— tubes, 53
Weights, 15
— tested, 16

ZINC, est., 197
— sep. from alkalies, 429
— sep. from alk. earths, *Index*, 430
— sep. from metals of Gr. III. and IV., *Index*, 433
— preparation, 94
— tests of purity, 94
— uses as reagent, 94
Zinc carbonate, properties, 128
— pp. in pure sols., 198
Zinc oxide, properties, 129
— conversion of zinc salts into, 199
Zinc sulphide, properties, 129
— conversion of zinc salts into, 200
— pp. in pure sols., 199.

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